STRUCTURE-PROPERTY RELATIONSHIPS OF THIOPHENE BASE
DERIVATIZED POLYMERS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1996

To my parents, brothers and sister.

ACKNOWLEDGMENTS

I am highly indebted to Dr. John R. Reynolds for his guidance and support throughout my graduate stay at the University of Florida. He has been a constant source of inspiration, and full of new ideas which made it exciting to do research in his group. It was an honor to work with him.

The support and discussions of my colleagues and friends, especially Peter Balanda, Dr. Seungho Kim, Dr. Myoungho Pyo, Dr. Michael diVerdi, Don Cameron, Anthony Pullen, Fernando Larmat, David Irvin, Jennifer Irvin, Gregory Sotzing, Jerry Reddinger and Shawn Sapp, are gratefully acknowledged.

I would also like to acknowledge the polymer floor people for making my stay productive and enjoyable; special thanks goes to the tireless Lorraine Williams for her help in getting all the paperwork done in time.

No words are enough to describe the four wonderful people, Srinagesh Kaushik, Narasimhan, K, Venkatramani, C. J. and Dinesh Patwardhan, who were my strength in United States.

Finally I would like to thank the Department of Chemistry for giving me this opportunity to come here to do my graduate studies.

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STRUCTURE-PROPERTY RELATIONSHIPS OF THIOPHENE BASE
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May 1996

The synthesis of 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene
(BTCMB), 3,4-ethylenedioxythiophene (EDOT), 5-octyldioxeno[2,3-c]thiophene
(EDOT-C$_8$) and 5-tetradecyldioxeno[2,3-c]thiophene (EDOT-C$_{14}$) and their
polymers are discussed in this dissertation. The chemical polymerization of
BTCMB yielded insoluble, brick red polymer with a decomposition temperature
of over 300 °C. Electropolymerization in CH$_3$CN with tetrabutylammonium
perchlorate yields electroactive and conducting films. Cyclic voltammetry of the
monomer showed two redox processes during the polymerization. The first
redox process has an onset at 0.8 V vs Ag/Ag$^+$ (peak = 0.9 V), while the
second has an onset at 1.0 V (peak = 1.1 V). When the potential is scanned to
0.9 V, very slow film formation is observed by cyclic voltammetry. Increasing the
switching potential of the scan up to 1.1 V leads to an increase in the rate of film
formation by nearly 25 times. This polymer is stable to electrochemical

switching up to 1.1 V. Optoelectrochemical studies showed that the highly oxidized polymer has only one absorbance in the NIR suggesting a metallic-like character.

Poly(3,4-ethylenedioxythiophene) and its alkyl derivatives show high absorbance (dark blue, opaque) in the visible region in their reduced, insulating state and significantly lower absorbance (light blue, relatively transparent) in their oxidized, conducting state. The band gaps (E_g) of poly[5-octyldioxeno[2,3-c]thiophene](PEDOT-C_8) and poly[5-tetradecyldioxeno[2,3-c]thiophene] (PEDOT-C_{14}) are 1.77 and 1.75 eV respectively. When these polymers are oxidized, at intermediate doping level, bipolarons are observed. In the highly oxidized state, these polymers also show only a single absorbance in the NIR suggesting metallic-like charge carriers. Long term switching studies of PEDOT and its derivatives were conducted in 0.1 M TBAP/CH$_3$CN, 0.1 M LiClO$_4$/CH$_3$CN and 0.1 M LiClO$_4$/PC. The substituted PEDOT's show faster switching times compared with unsubstituted polymer. When these polymers are switched in a well-defined reversible cell with Li as the counter electrode, they are stable to thousands of switches with over 45 % retention of their electroactivity. For example, PEDOT-C_{14} retains over 60% of its electroactivity after 16,000 double potential switches. PEDOT-C_{14} displays the maximum optical contrast between its reduced and oxidized state among these polymers. This high contrast suggests potential application of these materials in electrochromic devices.

1-1 History

When shiny silver polyacetylene films were discovered to conduct electricity after redox doping in 1977 by a group at The University of Pennsylvania, a new field of conductive polymers was started.[1] These polyacetylene films were synthesized by Hideki Shirakawa and coworkers with Zeigler-Natta polymerization on a glass surface,[2] and they were found to exhibit high conductivities. Naarmann and coworkers, in an improved synthesis, made polyacetylene that had conductivity similar to copper metal.[3] Unfortunately, the polymer film was brittle and extremely sensitive to the presence of water and oxygen.

One of the major structural criteria for a polymer to conduct is conjugation providing an overlap of π orbital electrons; this allows any charge formed to be delocalized along the polymer chain. Conductive polymers are insulators or semiconductors in their neutral form. In order for a conducting state to be formed, it is necessary to introduce charges by chemical or electrochemical oxidation or reduction. In the presence of an electric field these charges are mobile, and the polymer is an electrical conductor. The fascination of scientists with these new conductors motivated a significant amount of research in various aspects of conducting polymers. This work has been detailed in numerous review articles published in the literature.[4]

A practical thrust behind the development of organic polymeric conductors and semiconductors is the concept that polymers can be fabricated into electrical wires, films or other shapes without loss of conductivity, unlike conventional conductors and semiconductors. The light weight, relatively good mechanical strength, processability and corrosion resistance of these organic polymers are some of the factors that have created wide interest in such diverse fields as chemistry, physics, material science and chemical engineering.[5] This interdisciplinary research has been directed towards a common goal of developing organic conductors that have properties similar to, if not better than, standard inorganic conductors and semiconductors.

One of the major differences between inorganic and organic polymeric materials is the architectural designing ability of the molecule in organic chemistry. In organic polymeric materials, structural design is varied at the molecular level. This makes it possible to tailor a polymer according to the needs of the potential technological applications by fine tuning the molecular structure with changing of a functional group or the backbone of the polymer. This has lead to a better understanding of the relationship between the chemical structure of the repeat unit of the polymer to its mechanical and electrical properties.

Even though polyacetylene had a very high conductivity, its intractability and instability toward oxygen and water made it infeasible for commercialization. In 1979, the first free standing film of polypyrrole was electrochemically synthesized by oxidative polymerization of pyrrole. Though polypyrrole is flexible and stable to water and oxygen, it is intractable and insoluble. Then the electropolymerization was extended to other aromatic and heteroaromatic compounds including thiophene, furan, indole, carbazole, azulene, pyrene, benzene, fluorene.[6,7]

Polypyrrole,[6] polythiophene,[6] poly(phenylene sulfide),[6] polyphenylene,[8] poly(phenylene vinylene),[9] poly(thienyl vinylene),[10] and polyaniline[6] were chemically synthesized, and their electrical properties were studied. Among these, polythiophene exhibits an adequate stability in both its doped and undoped states making it potentially useful for the development of better materials. Thiophene is also structurally versatile, making it possible to derivatize to suit the needs of potential applications. Long alkyl chains substituted in the 3-position of the thiophene made the once insoluble polythiophene soluble without much compromise of its electrical properties.

Polyacetylene, polyphenylene, polypyrrole, polyaniline and polythiophene and their deivatives are the most extensively studied electroactive polymers. In the following paragraphs, a small snynopsis of these polymer's evolution to obtain soluble material is outlined.

1.2 Polyacetylene

Shirakawa and coworkers were the first to synthesize polyacetylene using a thin coating of a hetrogeneous Ziegler-Natta initiator system in a glass reactor as shown in the Figure1.1.[1,2] Polyacetylene sythesized in this manner

$$n \quad H-C{\equiv}C-H \quad \xrightarrow{\begin{array}{c} Al(C_2H_5)_3 \\ \hline Ti(OC_4H_9)_4 \end{array}} \quad \left[\diagup \!\!\!= \!\!\! \diagdown \right]_n$$
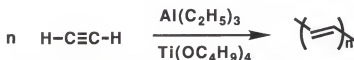
Figure 1.1: Shirakawa's synthesis for polyacetylene.

was highly crystalline, fibrillar and also very insoluble. When this synthesis is carried out at -78°C, the polyacetylene obtained is in the form of the cis-transoid isomer. By heating the cis-transoid isomer to 150°C, it can be isomerized to trans-transoid, which forms lustrous, silvery films that are thermodynamically

more stable than the cis-transoid isomer. Different types of initiator systems[11] or annealing and aging[12] of the catalyst led to improvements in the stability and type of polyacetylene film formed. While this improvement decreases the amount of defects in the film, it is still completely non-processable.

Since the polyacetylene formed was intractable, a soluble precursor polymer route was developed. One of the most highly studied systems utilizing the soluble precursor method is shown in Figure 1.2. The metathesis
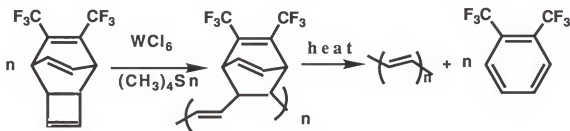
Figure 1.2: Metathesis polymerization *via* soluble precursor to synthesize polyacetylene.

polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-triene using WCl_6 and CH_3Sn was developed to provide a soluble precursor polymer that can be subsequently converted to $(CH)_x$ thermally.[13] This precursor is useful in the production of thin films. The thermal conversion step is highly exothermic and potential explosion hazard. The $(CH)_x$ films formed were much more dense and less fibrillar than the material made from Shirakawa's technique. The polymer obtained after elimination was amorphous, but stretching of the film during the thermal elimination lead to highly oriented and crystalline material.[14]

One of the deficits of this soluble precursor was that a large molecule had to be thermally eliminated during the conversion. This leaves void spaces in the polymer films and the elimination is not quantitative. To overcome this

Grubbs and coworkers utilized ring opening metathesis polymerization (ROMP) to obtain a strained precursor, which will easily isomerize to yield $(CH)_x$ as shown in Figure 1.3.[15] ROMP of benzvalene results in polybenzvalene, which has a bicyclobutane ring in the main chain. This ring can be thermally isomerized to obtain $(CH)_x$. The polymeric material obtained has fibrillar morphology and saturated defects along the backbone.

Benzavalene   Polybenzvalene
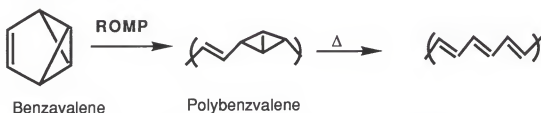
Figure 1.3: ROMP of benzvalene to yield polyacetylene.

To improve the solubility of polyacetylene, substituent groups can be attached.[16] ROMP of substituted cyclooctatetraenes provides a convenient route to a variety of substituted polyacetylenes whose properties vary with substituent. ROMP of trimethylsilylcyclooctatetraene yielded a soluble polymer as shown in Figure 1.4.[17] The substituent groups break the conjugation, and

Figure 1.4: Synthesis of soluble polyacetylenes
by ROMP of trimethylsilane substituted
cyclooctatetraene

hence the conductivity is lower than the Shirakawa polymer. The solubility of this polymer allows the study of solution properties, which was impossible with the earlier polyacetylenes. Many substituents were attached to this polymer,

and their molecular weight , conductivity, spectroscopic and other properties were investigated.[18]

Domains of polyacetylene can be introduced into soluble polymeric materials to aid processing. This can be achieved either by grafting $(CH)_x$ chains onto a carrier polymer or by making block copolymers with a soluble segment. An example of the graft polymerization is shown in Figure 1.5.[19] Polybutadiene has 1,2 and 1,4-diene linkages. The 1,2 linkage leads to a vinylic group as a side chain. This vinylic group is utilized to graft polyacetylene to the main polybutadiene chain using Ziegler-Natta conditions. This will lead
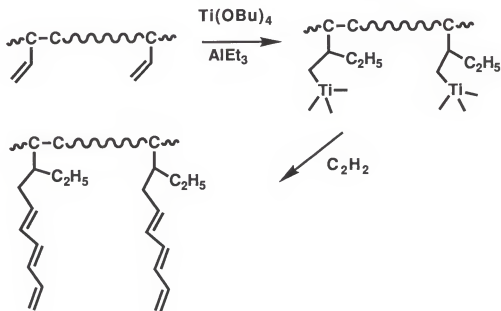
Figure 1.5: Grafting polyacetylene onto polybutadiene backbone.

to domains of polyactylene in the polymer backbone. Similarly, blocks of polyacetylene can be incorporated into a soluble polymer backbone by copolymerizing acetylene with another living polymer. The types of copolymerization are increased by the ability to change the nature of the active site after the synthesis of the first block by one mechanism and subsequently

use different propagation mechanism to attach the second block.[20] For example, polystyrene prepared by anionic polymerization to obtain a living site can be utilized to copolymerize acetylene *via* Ziegler-Natta type polymerization as shown in Figure 1.6. After forming the living polystyrene anionically, the initiator $Ti(OBu)_4$ is added to the reaction mixture. One of the butoxide groups reacts with the lithium ion to form LiOBu, and $Ti(OBu)_3$ attaches to the living site of polystyrene. By losing one of the butoxide groups, Ti metal now has an active site to receive an acetylene molecule to polymerize.
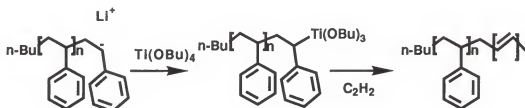
Figure 1.6: Anionic followed by Ziegler-Natta polymerization
of polystyrene with acetylene

1-3 Polyaniline

Polyanilines are a large class of conducting polymers which exist in three different discrete oxidation levels both in their doped and undoped forms.[21] Mixtures of these oxidation states are readily obtained. One of these discrete oxidation states can be doped by a non-redox process without adding or removing electrons from the polymer backbone. The reduced form of polyaniline can also be doped by a conventional oxidation process.
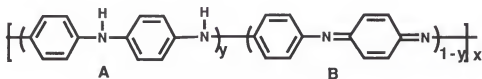
Figure1.7: The base form of polyaniline

General composition of the base form of polyaniline is shown in Figure 1.7.
Polyanilines consist of alternating reduced (**A**) and oxidized (**B**) repeat units.[22]
The average oxidation state, 1-y, can be varied from 0 to give completely
reduced polymer, to 0.5 to give half oxidized polymer, and to 1.0 to give
completely oxidized polymer. When the oxidation is 0, 0.5 and 1.0, these states
are called as leuco-emeraldine, emeraldine and pernigraniline respectively.

The emeraldine base form (Figure1.8) can be protonated to obtain the
emeraldine hydrochloride salt.[23] The imine nitrogen can be protonated in
whole or in part. Complete protonation of the emeraldine base results in the
formation of a radical cation, and in this form the polymer has the highest
conductivity. The number of electrons associated with the polymer after the
doping (protonation), is the same as in the undoped material, and the
processability of the polymer makes it an interesting polymer to study.

Emeraldine Base

2x HCl
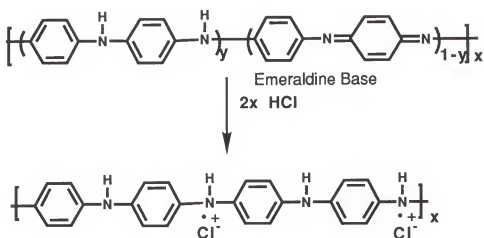
Figure 1.8: Protonated emeraldine hydrochloride salt

1.4 Polyphenylenes

Polyphenylenes exhibit high heat resistance in the neutral form and electrical conductivity on doping.[24] The most important polyphenylene is the poly*para*phenylene, PPP. An ideal poly(1,4-phenylene) would possess high molecular weight, all *para*-linked chains, which would have excellent thermal stability and conductivity. However, direct synthesis of polyphenylenes leads to totally insoluble, intractable solids. One of the first successful polyphenylenes synthesized from benzene was reported by Kovacic and coworkers.[25]
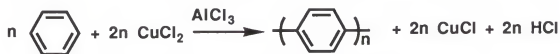
Figure 1.9: Polymerization of benzene

Benzene polymerization was carried out using $CuCl_2$ as the oxidizing agent to obtain the polyphenylene with a degree of polymerization (DP) *ca.* 10. This polymer was slightly soluble in THF (Figure 1-9). The condensation of 1,4-
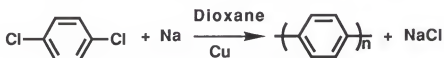
Figure 1.10: Polyphenylene via Wurtz-Fittig reaction

dihalobenzene using alkali metals and copper powder (Figure 1.10) yielded low molecular weight products with irregular structure.[26] Yamamoto and coworkers used a different catalyst and very mild conditions as shown in Figure 1.11.[27] They made a mono Grignard of 1,4-dibromobenzene and condensed it in the presence of $NiCl_2$(bpy). The product was regular poly(1,4-phenylene)

with no defects. This method resulted in higher yields and higher DP's, but the dibromobenzene monomer is much more expensive than benzene. A modified Ni catalyst, Ni(cod)$_2$ (cod: 1,5-cyclo-octadiene) was used by the same researchers, resulting in higher yield and DP of the PPP polymer.[28]
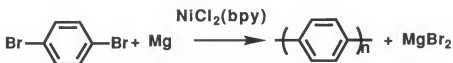
Figure 1.11: Yamamoto condensation reaction to synthesize polyparaphenylene.

To overcome the insolubility of PPP, a soluble polymer precursor route was employed. Benzene was subjected to bacterial oxidation using the microorganism *Pseudomonas putida* to prepare the 5,6-*cis*-dihydroxycyclohexa-1,3-diene. The dihydroxycyclohexadiene was esterified and then radically polymerized to obtain a soluble PPP precursor, as shown in
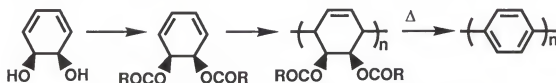
Figure 1.12: Soluble precursor route to synthesize high MW PPP.

Figure 1.12.[29] Different types of ester groups were attached to obtain high thermal conversion, resulting in higher DP. Another route to a obtain soluble PPP precursor was, by using 2-carbomethoxy-1,4-dichlorobenzene as shown in Figure 1.13.[30] 2-carbomethoxy-1,4-dichlorobenzene was polymerized using Ni(0) as the catalyst in DMF. Saponification of the PPP-ester produced PPP-carboxylic acid. This was soluble in pyridine, quinoline and NaOH. In the presence of CuO and heat, the precursor decarboxylated to yield PPP. The DP

in this reaction was close to 100, and good PPP films were obtained using this precursor route.

Unfortunately, none of the final polymers obtained in the above reaction were soluble. Hence a new polymerization technique was developed where A-B step-growth polymerization lead to soluble PPP as shown in Figure 1.14.[31]
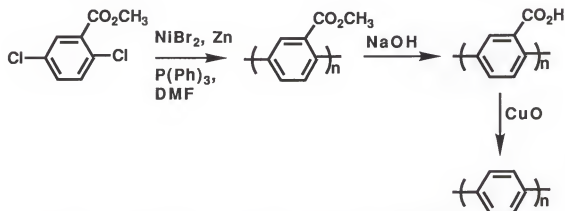
Figure 1.13: Synthesis of soluble acid PPP precursor to obtain PPP.

The difunctional monomer is coupled in presence of heterogeneous Pd(0) catalyst and aqueous Na_2CO_3 to yield the soluble PPP.
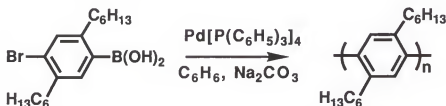
Figure 1-14: Pd catalyzed boronic acid coupling reaction.

1-5 Polypyrrole

Polypyrrole is a heteroaromatic polymer having an oxidation potential lower than PPP or polythiophene. Pyrroles can be chemically or

electrochemically polymerized to yield an insoluble black solid.[32] Polypyrrole
is very stable in the oxidized, conducting state and highly reactive with air in the
reduced, insulating state. Extensive electrochemical studies of polypyrrole
have been carried out leading to many potential uses of polypyrrole in
batteries, sensors, as a biocompatible polymers, electromagnetic shielding, as
a coating on textiles etc.[33] Limited work has been done on derivatization of
polypyrroles and property investigation of the deivatized pyrroles.

<h3 style="text-align:center">1-6 Polythiophene</h3>

Polythiophene is an insoluble, heteroaromatic macromolecule, having an
oxidation potential lower than that of PPP. Thiophene has been polymerized
using a number of routes to obtain a polymer which is blue black in its
conducting, oxidized form and brick red in its reduced insulating form. Attaching
a long alkyl chain to the backbone of an intractable polymer chain improves in
the dissolution of the polymer. On thiophenes, substituents can be attached at
the β-carbon atom before polymerizing to make the polymer soluble and fusible.

Soluble poly(3-alkylthiophenes) were first synthesized in 1986.[34-37]
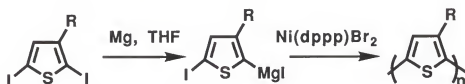
Figure 1-15: Ni catalyzed Grignard coupling reaction to
synthesize soluble polythiophenes

Elsenbaumer *et al.* prepared the methyl, ethyl, butyl and octyl substituted
poly(3-alkylthiophenes) *via* a chemical route as in Figure 1-15. They prepared
in situ the monoiodo-Grignard reagent from 3-alkyl-2,5-diiodothiophene and
coupled using nickel catalyst. Among the poly(3-alkylthiophenes) obtained,

poly(3-octylthiophene) had the best solubility. Films of the polymer were easily cast to study its properties. This chemically prepared polymer has a regular linear structure with only $\alpha-\alpha$ linkages and no cross linking. Both the electrochemically polymerized and chemically polymerized (via oxidative coupling with $FeCl_3$) 3-alkylthiophenes resulted in cross-linking of the polymer through the β carbon atoms. These give rise to defects in the polymer chains, affecting the electrical and electronic properties of the polymer. Though the poly(3-alkylthiophenes) synthesized as per Figure 1-16 have a regular linear structure, they are still not regiospecific with respect to the alkyl chain attached. The Grignard can form at the 2 or 5- position, making the eventual polymer regio-irregular. The ratio of head-tail to head-head isomer is 63:37. The removal of these defects was expected to increase the conductivity of the polymer by at least two orders of magnitude.

To synthesize regio-regular poly(3-alkylthiophenes), McCullough and coworkers developed a new synthetic method.[38] They started with 2-bromo-3-alkylthiophene as shown in Figure 1-16. The proton at the 5-position was
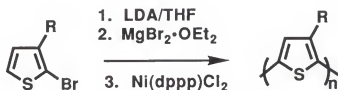
Figure 1-16: Regioregular poly(3-methylthiophene)
by Ni catalyzed Grignard coupling reaction

specifically removed by using LDA, and that position was converted into a Grignard site by adding $MgBr_2 \cdot$dietherate. This was coupled with Ni catalyst to yield a high degree (over 96 %) of regio-regularity in the back bone of the

polymer. Similar methodology to obtain regio-regular polymer was used to synthesize poly(3-hexylthiophene-2,5-diyl).[39]

1.7 Mechanism

1-7-1 Mechanism of polymerization

The oxidative polymerization of a heterocyclic monomer leading to a conjugated polymer can be performed chemically and electrochemically. Chemically the polymerization is done *via* oxidative-coupling reactions. The mechanism of the polymerization is not yet completely understood, but studies relating to elucidation of the mechanism have recently been published.[40] Electrochemistry has been a very important analytical tool used to study the mechanism of heterocycle polymerization.

A simplified form of the elecrochemical sysnthesis mechanism is shown in Figure 1.17.[41] The initial step involves the anodic oxidation of the monomers close to the surface of the electrode. The oxidation leads to the formation of a radical cation.[42] This radical cation can dimerize by adding to another radical cation, as shown in Route A, or it can lose a proton to form a radical which can either combine with another radical to form a dimer, as shown in Route B, or add to another monomer, as shown in Route C. This initial step is very fast, and there is not enough evidence to unequivocally point toward either route, but there is evidence to suggest these steps.

An electron loss leading to the formation of a radical cation is now widely accepted as the initial reaction. The presence of radical cations was confirmed by ESR experiments on thiophene systems;[43] the radical cation is stable for several seconds. Addition of trifluoroacetic acid to the electrolytic medium
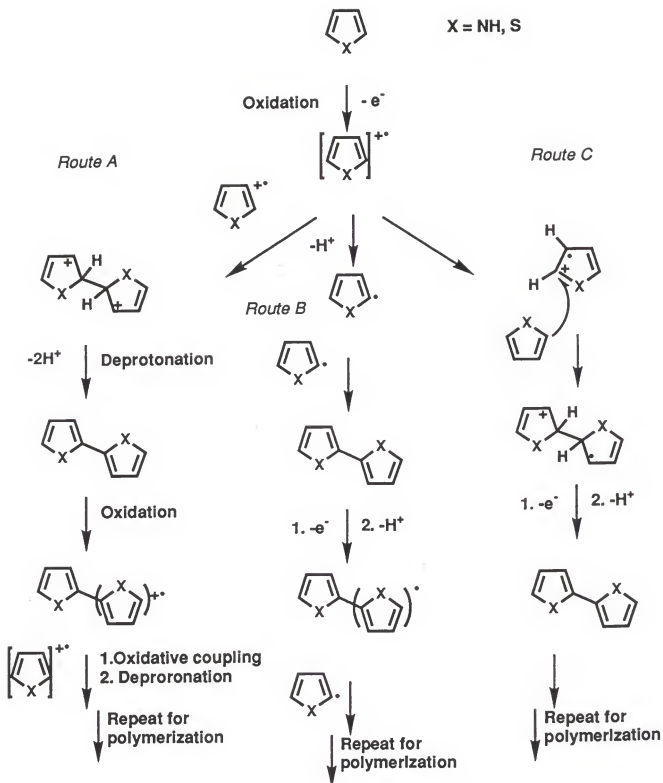
Figure 1.7a: Polymerization mechanism for heterocycles.

increases the lifetime of the radical cation formed to several hours.[44] Though the disproportionation of the proton is very slow, for a neutral solution there may be some disproportination, leading to the *RouteB* type of mechanism. To disprove the proton disproportionation hypothesis, Savéant and coworkers added a 100 mM base (2,6-di-*tert*-butylpyridine) to their 5 mM pyrrole system during cyclic voltammetric experiments with scan rates ranging between 200 and 2000 Vs^{-1}.[45] The addition of base had no noticeable effect on the voltammogram, giving credence to *Route A* as the plausible mechanism.

Wei *et al.* have proposed an alternate mechanism to Roures A and B based on results from the following experiments.[46] In the 0.2M 3-methylthiophene electrolytic system, a small amount of 0.5 to 2 mM of 2,2'-bithiophene (dimer) was added before polymerization. This addition led to an increase in the rate of polymerization. This increase in rate was sustained until the polymerization was stopped. The voltage required for the polymerization is lower than the oxidation potential of 3-methylthiophene, suggesting that the 2,2'-bithiophene acts as an initiator. A similar increase in the rate of polymerization was observed when 2,2':5'2"-terthiophene (trimer) was added. This observation lead to the suggestion of *Route C*. In this proposed route, the neutral monomer reacts with the radical cation in an electrophilic addition manner. This adduct then loses an electron and two protons to form a neutral dimer. This disproportion step is believed to produce an acidic environment in the region around the anode.[47] The dimer loses an electron to generate a new radical cation, and the reaction is repeated.[48] Though this experiment suggests that there is an electrophilic addition during polymerization, it is still not clear whether the same effect is dominant for the polymerization of the monomer without the addition of any oligomers. In this polymerization, a constant

potential must be applied to form the polymer; this strongly suggests that the mechanism follows *Route A*.

The growth of the polymer on the surface of the electrode is preceeded by nucleation.[49] When the potential is applied in the electrochemical synthesis, the monomer in the vicinity of the electrode is oxidized and combines to form dimer. As the synthesis is continued, the oligomers precipitate onto the electrode when they attain a certain length exceeding the solubility limit.[50] Since these are conducting polymers, they serve as a nucleation site for more polymer to grow on. The growth is normally one-dimensional, since growth perpendicular to the electrode surface is more rapid than across the surface.[51] In the electropolymerization of pyrrole, the polymer grows more in one direction, leading to large number of nucleation sites on the electrode surface. This increases the number of polymer chains, and the polymer film formed is more dense and uniform.

1-8 Band Theory

1-8-1 Redox Switching of Polymers and Theory of Conduction

Conjugated polymers in their neutral form are insulators, and to make them conduct, charge carriers must be created. Conducting polymers have the ability to be switched reversibly between oxidized and reduced states as shown in Figure 1-18. The switching is done in the presence of an electrolyte to provide counter ions to stabilize the charges formed on the backbone of the polymer.

Conjugated polymers have π orbitals which overlap throughout a chain if the chain is planar. The conduction in these types of polymers is due to the movement of the charge carriers along the backbone of the polymer and also
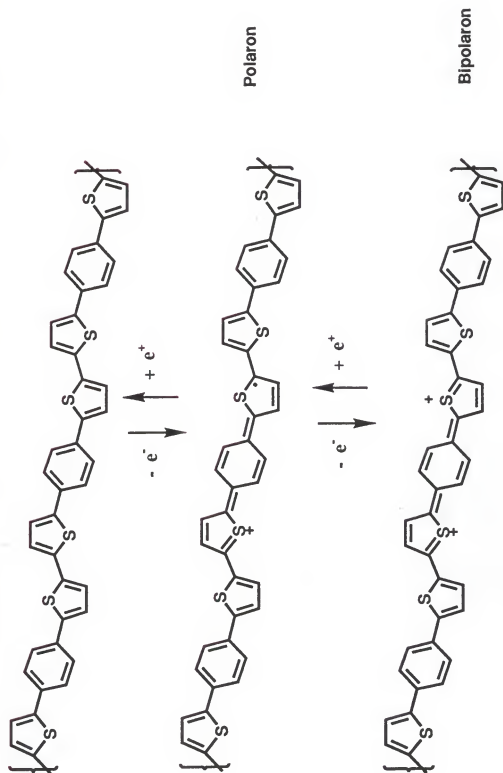
Figure 1.8a: Redox switching behavior of poly[1,4-bis(2-thienyl)phenylenes]
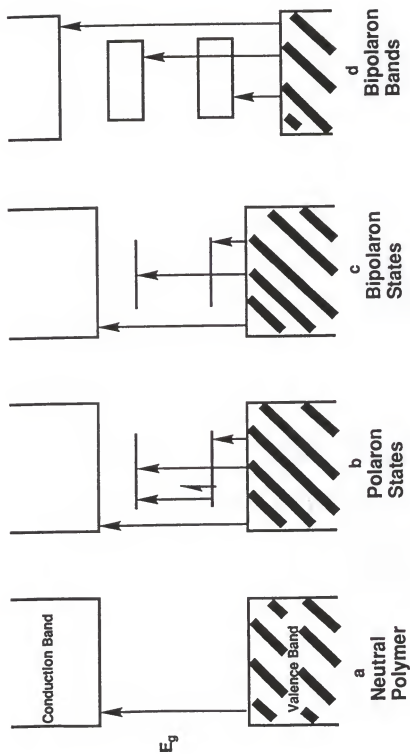
Figure 1.8b: Band diagram for the doping effect on conducting polymer for non-degenerate ground states.

due to the hopping of these charges between chains. Since the π orbitals are orthogonal to the plane of the molecule, the more planar the molecules in the conduction state, the better the conductivity. More planar molecules also result in better stacking of the polymer chains, leading to better overlap among chains and higher conductivity by inter-chain hopping of the charges.

Figure 1-19 depicts a simplified version of the theory of conduction.[52,53] The bonding and anti-bonding π molecular orbitals of the polymer consist of a large number of energy levels, with a very small difference in energy between any two consecutive levels. These energy levels are combined and depicted as bands called valence and conduction bands. The difference between the highest occupied molecular orbital (HOMO) in the valence band and the lowest unoccupied molecular orbital (LUMO) of the conduction band is the energy gap or band gap (E_g) of the polymer. In the neutral form, the energy gap is high, and the polymer is an insulator. As the polymer is oxidized by removing an electron from the polymeric system, a radical cation, called polaron, is generated, resulting in a distortion of one of the energy levels, raising one of the energy levels from the HOMO and lowering an energy level from the LUMO. When another the electron from the polaron state is removed, the polymer forms a dication, called bipolaron. As the oxidation is continued, the intermediate levels in the bipolaron states continue to increase, eventually forming bands called bipolaronic bands. The intermediate levels in the bipolaronic bands are much closer to the valence band than to the conduction band. Hence, it is easier to excite an electron into one of these levels, leading to conduction.

1-8-2 Degeneracy

Polyacetylene has a low band gap and high conductivity. One of the reasons for this is its degeneracy,[54] although the C-C double and single bonds

are of different lengths. The smaller this bond length alternation, the smaller the band gap. If these bond lengths can be made equal, then the band gap will vanish.[55]

Systems like polypyrrole, polythiophene and polyparaphenylen possess a non-degenerate ground state (as shown for polyparaphenylene in Fig. 1-20). The aromatic-type of geometrical structure is expected to dominate for these systems. A quinoidal-type structure would have higher energy. *Ab initio* calculations made by Bredas for a polythiophene system showed that a quinoidal structure will have lower ionization potential and higher electron affinity than an aromatic structure.[56] With the help of Valence Effective Hamiltonian (VEH) calculations, Bredas demonstrated that the linear decrease in the band gap value is not a function of reduced bond length alternation but a function of increasing quinoidal character of the geometry.
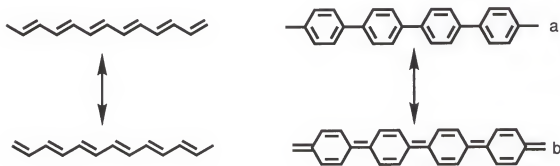
Figure 1-20: Degeneracy of polyacetylene and non-degeneracy of polyparaphenylene because of higher energy content of b compared to a.

Polyacetylene is unique among all other conducting polymers. Like any other conjugated polymers, polyacetylenes can also be redox doped to induce charge carriers. Due to its degeneracy, the charge is highly delocalized. When polyacetylene is doped, (reduced or oxidized), instead of generating two intermediate states in the bipolaronic bands, it creates only one intermediate

level exactly mid way between the valence and conduction bands. This doped state, called soliton, is shown in Figure 1-21.[57,58] The energy on both sides of the charge is the same except for the phase change in the orbitals. The charge is free to move up and down the chain without needing to overcome any energy barriers. This is not the case for all aromatic polymeric systems. When an aromatic conjugated polymer is doped, the resulting charged polymer has to

Soliton
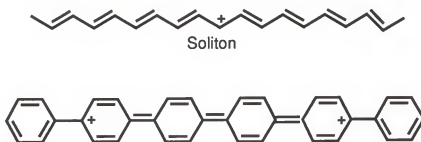
Figure. 1-21: Doped polyacetylene and polyparaphenylene

undergo a change in the structure from lower energy aromatic form to the higher energy quinoidal form as shown in Figure1-21. The quinoidal form will try to revert back to the aromatic form. In highly oxidized polyaromatic systems, where there are a large number of charges, this collapse of quinoidal forms will eventually bring two charges closer to each other. Since they are similar charges, they repel each other. This repulsive force and energy difference between aromatic and quinoidal forms controls the number of aromatic rings between any two charges in a conjugated aromatic polymeric system.

1-9 Electrochromism

1-9-1Background

Electrochromism is a phenomenon in which there is a persistant optical absorbance change in the visible region of the spectrum with the application of an external potential. An electrochromic device is an electrochemical cell in which electrochromic material coated on an electrode is separated by an electrolyte from the charge-balancing counter electrode. This phenomenon has been known since 1969.[59] Most of the electrochromic materials studied at that time were inorganic oxides like tungsten and vanadium oxides.[60] The electrolytes used to study these materials or to make devices were inorganic salts of Li and Fe. The introduction of organic polymers in the study of electrochromic materials started by using polymer-based electrolytes like poly(2-acrylamido-2-methylpropanesulfonic acid)[poly-AMPS], polyvinylpyrrolidone[PVP] and polyethyleneimine [PEI]. These were pioneered by Giglia and Haacke,[61] and Randin and Viennet.[62] The goal of this research was to obtain an electrochromic display. As in any electrochemical cell, these display devices had to have two electrodes and an electrolyte to carry the charge. Both the electrodes were coated with thin films of inorganic oxides, and a supporting electrolyte dissolved in a solvent was used to carry the charge. The use of solvents led to sealing problems in the device, since the solvents were free-flowing. To overcome this, polymer gels like polyethyleneoxide (PEO), polymethylmethacrylate (PMMA), etc. were used instead of solvent .

1-9-2 Organic Electrochromic Materials

Viologen was one of the first organic materials used for the study of potential application for electrochromic properties.[63] Derivatives of viologen have been made to vary electrochromic properties. To obtain different colors, various derivatives of viologen were mixed together in solution, since they all

have different thresholds for coloration. Chung and Leventis from Molecular Displays used viologen and ferrous salts to make an electrochromic device.[64] The reactions leading to the change in coloration are shown in Figure 1-22. Viologen was coated onto one of the electrodes, and Everitt's salt imbedded polypyrrole was coated onto the other electrode with an aqueous polymeric gel electrolyte between them. Viologen, which is a colorless salt, becomes deep violet when reduced. At the same time at the other electrode, the colorless Everitt's salt [Fe(II)] changes to blue upon oxidation. Many derivatives of the viologen have been studied to obtain different colors.

$$K_4Fe_4[Fe(CN)_6]_3 \longrightarrow 4e^- + 4K^+ + Fe_4[Fe(CN)_6]_3$$

Everitt's salt [Fe(II)]
colorless

Prussian blue [Fe(III)]
blue
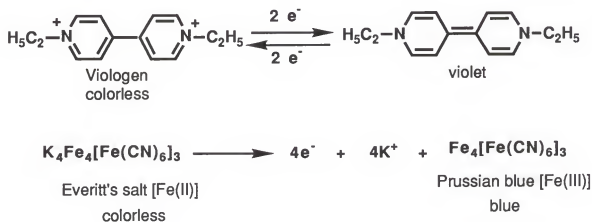
Figure 1-22 : Chemical reactions at both the electrodes of a viologen based electrochromic device.

1-9-3 Transition Metal Complexes

Most of the materials studied for electrochromic properties undergo a chemical change, like a change in oxidation state, during the phenomenon. Abbott and coworkers at University of Leicester in England have made semiconducting organic and organometallic complexes, like CuMNT and TTF as shown in Figure 1-23, that change their absorbance wavelength in the visible region when an electric potential is applied across them.[65] The change

in absorbance wavelength for these materials was caused by a physical rather than a chemical change. This work is unprecedented, since this is a physical phenomenon, and there is a necessity for the ions to be non-centrosymmetric. The application of potential seems to allign the ion-dipoles within the lattice, changing the overlap of the molecular orbitals and therefore changing the absorbance. When the potential is removed, the spectrum does not revert back to its original form, but reversion does occur when the material is annealed in an oven at 100 °C for 30 minutes.

Disodium copper maleonitrile dithiolate complex anion
with methylbenzylammonium cation (CuMNT)

Tetrathiafulvene complex cation
with mandelate anion (TTF)
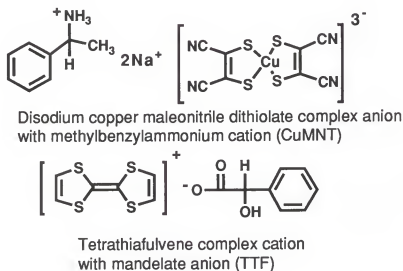
Figure 1-23: Transition metal complex
and organic electro-optic material

1-9-4 Organic Polymers

The inorganic oxides and organic salts used are coated or electroplated onto an ITO glass plate. After application of a potential, the individual molecules contribute to the change in absorbances. The optical memories of individual molecules are different, and the retention time of one of the states by these molecules varies. Hence there is less uniformity across a film and more chances of a defect in the film. To overcome this, electrochromic materials were

attached to polymer chains. One of the earlier examples of this was polystyryl with TTF[66] or pyrazoline[67] as pendant groups as in figure 1-24.[68]
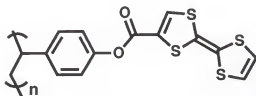
Figure 1-24: TTF based polystrylester.

As the polymer is oxidized, the color of the film changes from pale yellow to green to purple, as TTF goes first to TTF^{+1} and then to TTF^{+2}. Different derivatives of TTF pendant polymers were synthesized to study their electrochromic properties. Similar to this type of polymer, Shirota and coworkers synthesized polyethylene with terthiophene as a pendant group at every other carbon atom.[68] This polymer turns blue when oxidized, while in the reduced state it is nearly colorless. In the reduced state the polymer is very soluble like any other substituted polyethylene.

The color contrast in the oxidized and reduced states can also be controlled by the effective conjugation length of the polymer chain. This color contrast can be tailor made by using oligomers of a parent molecule for polymerization as shown in Figure 1-25. Mastragostino and coworkers used thiophene and methylthiophene to make dimers and tetramers, which were then electrochemically polymerized and studied spectrochemically.[69] Depending upon the oligomers used for the electropolymerization, the effective conjugation can be varied, due to steric demands of the methyl groups at different positions. This leads to a change in absorbance of the eventual polymer in both the states.

Polyaniline,[70] polyisothianapthene,[71] poly(N-methylisoindole),[72] and polycarbazole[73] are some of the other polymeric materials that are used to study the electrochromic behavior in conjugated systems. Copolymers of conjugated systems like copolymers of aniline and N-alkylaniline are being synthesized to tailor properties such as color, switching speed and switching response.[74]
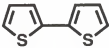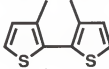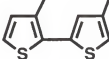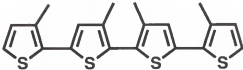
Monomer molecules	Color of the polymer	
	Doped	Undoped
	Orange	Blue
	Yellow	Violet
	Red	Blue
	Yellow	Blue

Figure 1-25: Color contrast of thiophene based polymers in their oxidized and reduced states

1-10 Synopsis of my Work

This dissertation entails the study of structure-property relationships of thiophene based polymer derivatives. Polythiophene, being the most stable among the conjugated systems in both oxidized and reduced states, is the

choice as the parent polymer. Two types of derivatives, with the thiophene moiety within the back-bone, are synthesized to investigate these structure-property relationships. These polymeric conjugated systems are electroactive in nature.

The first polymer is obtained by derivatizing thiophene, to yield a symmetrical monomer, 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene. Chemical and electrochemical syntheses was carried out on this monomer. Electrochemical and optoelectrochemical studies were conducted on this monomer and polymer.

The second type of derivatizaton was done by fusing a dioxane ring on to the 3,4 position of the thiophene ring, thereby lowering the oxidation potential of thiophene and also blocking the 3 and 4 positions from being a polymerization site. Three different types of monomers, 3,4-ethylenedioxythiophene, octyl and tetra-decylsubstituted 3,4-ethylenedioxythiophenes were synthesized. These monomers were electrochemically polymerized in different electrolyte/solvent systems and their properties studied. Optoelectrochemistry of these polymers was investigated to determine the band gap and evolution of charge carriers as a function of voltage. Long term switching studies were conducted and the switching stability and rates of all three polymers are compared. An attempt is made to determine the density and molar absorptivity of these polymer films to determine the type of electronic transition that is occuring in these films when irradiated with light.

SYNTHESIS AND ELECTROCHEMISTRY OF POLY[1,4-BIS(2-THIENYL)-2,5-
DICYCLOHEXYLMETHYLOXYPHENYLENES]

2-1 Background of Poly[1,4-bis(2-thienyl)-2,5-disubstitutedphenylenes]

The structural modification of conjugated polymers by the attachment of
flexible substituents has proved effective in introducing solubility and fusibility to
the intrinsically insoluble and intractable backbones. As examples, soluble
derivatives of polythiophene,[75] polypyrrole[76] and poly(*p*-phenylene)[77] have
been reported. Substitution with sufficiently long alkyl chains has led to the
production of true thermoplastic materials which can be processed using both
solution and melt methods. When the substituents are ionic in nature,
conjugated polyelectrolytes are formed which can be water soluble.[78]

In addition to the introduction of processability, substitution of conjugated
polymers has been shown to exert a strong influence on the optical, electrical,
and electrochemical properties of these polymers. The Reynolds group[79] and
others[80] have been probing these effects in our studies of the poly[1,4-bis(2-
heterocycle)-*p*-phenylenes] (PBHP's) by changing backbone and substituent
structures. The electron donating nature of alkyl and alkoxy substituents has
been shown to lower monomer and polymer oxidation potentials, and reduce
the optical band gap by increasing the electron density in π conjugated
systems.[81] Pendant substituents have also been shown to have a strong steric
influence on the conformation of the conjugated backbone. Steric repulsions
between pendants on adjacent rings results in an increase in the energy barrier
to planarity of the ring system. Since a high degree of conjugation is necessary

for charge carrier transport, this torsional strain leads to an increase in oxidation potentials and a decrease in electrical conductivity. This effect is demonstrated by poly(1,4-bis(2-thienyl)-2,5-dimethylphenylene), where the thiophene-phenylene torsional angle has been calculated to be significantly larger than the unsubstituted, or dimethoxy, analog.[79a] More importantly, the energy barrier to planarity increases from 3.1 kcal/mol to 15.8 kcal/mol with methyl substitution. This results in an increase in both the monomer and polymer oxidation potentials and decrease in conductivity of more than 5 orders of magnitude.[79a]

The studies of the PBHP's were initially motivated by the potential for improved solubility of the polymers relative to non-derivatized conjugated polymers. The desirable electronic properties of the polyheterocycles are combined with the ease of substitution of the phenylene ring. At the same time, the monomers can be symmetrically derivatized yielding isoregic polymers with enhanced order.[80b] It is now accepted that higher degrees of long range order can lead to significant enhancement of electrical conductivity.[75b]

In the PBHP's, it has been found that, although the parent polyheterocycle properties are largely retained, some unique electrochemical phenomenon are observed in both monomers and polymers. This chapter reports synthesis and electrochemical studies of a new derivative to this series containing cyclic alkoxy pendants, poly[1,4-bis(2-thienyl)-2,5-dicyclohexyl-methyloxyphenylene] (PBTCMP), which displays two oxidation waves in the cyclic voltammogram of its monomer. This behavior is absent in the other substituted derivatives of poly[bis(2-thienyl)phenylene] series, and microgravimetric analysis suggests that it is due to solubility of the deposited oligomers. PBTCMP shows only one at low energy electronics transition at high oxidation potential, displaying characteristics of metallic-like charge carriers.

2-2. Synthesis

2-2-1. Monomer, 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene, (BTCMB)

The monomer, 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxy-benzene was synthesized using methods developed to synthesize other bis(2-heterocycle)benzenes as shown in Figure 2-1. Hydroquinone was deprotonated with alcoholic KOH and dialkylated by drop-wise addition of 1-bromomethyl-cyclohexane. This 1,4-dicyclohexylmethyloxybenzene was brominated at the 2 and 5 positions by drop-wise addition of bromine in $CHCl_3$ to yield 2,5-dibromo-1,4-dicyclohexylmethyloxybenene, and subsequently reacted with 2-thienyl-zinc chloride to yield 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene.

Figure 2-2 illustrates the ^{1}HNMR of the BTCMB. Resonances for the aromatic hyrogens are all above 7.0 ppm, for the methylene and cyclohexyl part are at 3.9 and between 1.0 to 2.0 ppm respectively. The integration of the resonance peaks are proportional to the required number of protons. The ^{13}CNMR for the monomer as seen in Figure 2-3, has four resonances between 25 and 39 ppm for cyclohexyl carbons, one resonance at 75.9 ppm for methylene carbon and seven resonances for the aromatic carbons of the thiophene and benzene moiety. The molecule is symmetrical across the plane of benzene.

2-2-2. Chemically prepared Poly[1,4-bis(2-thienyl)-2,5-dicyclohexyl-methyloxyphenylene] (PBTCMP)

The $FeCl_3$ induced oxidative polymerization of BTCMB, followed by compensation with aqueous NH_3 yielded a brick red neutral polymer that was
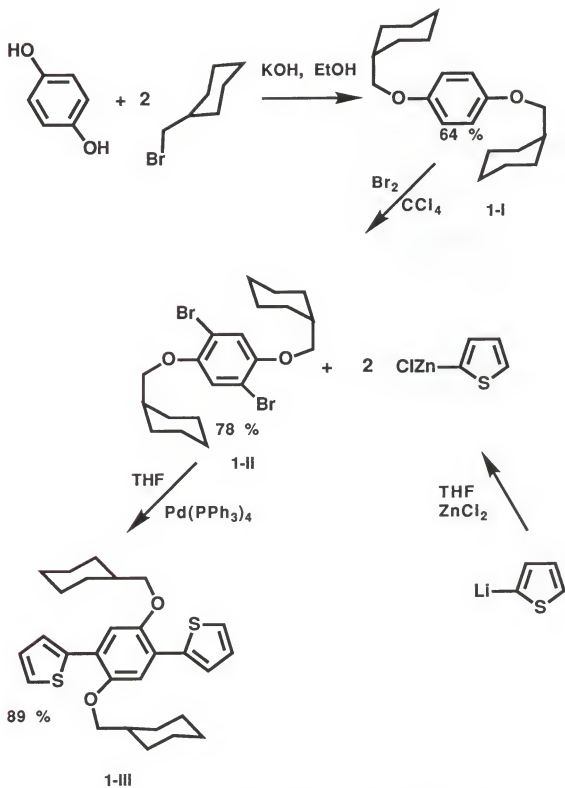
Figure 2-1: Synthetic scheme for the monomer 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene.
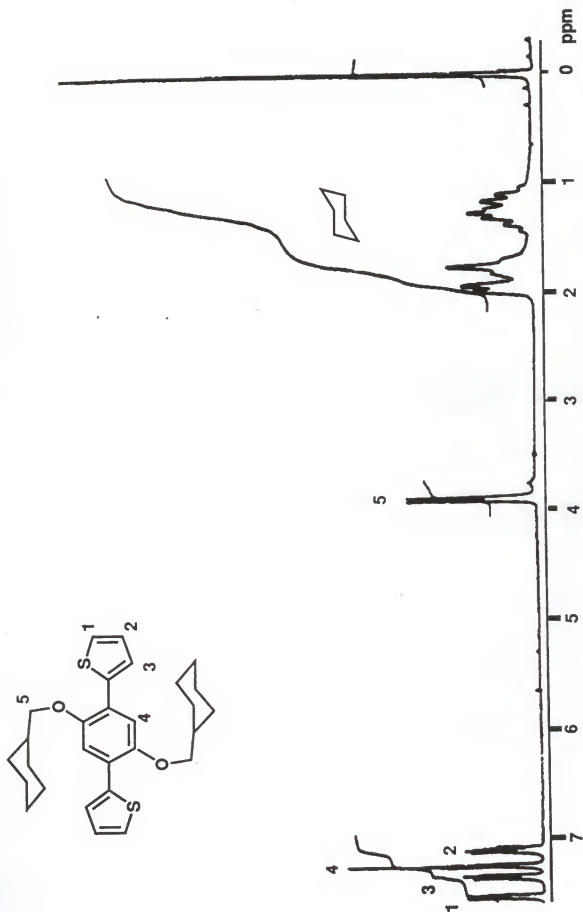
Figure. 2-2: 1HNMR of 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene
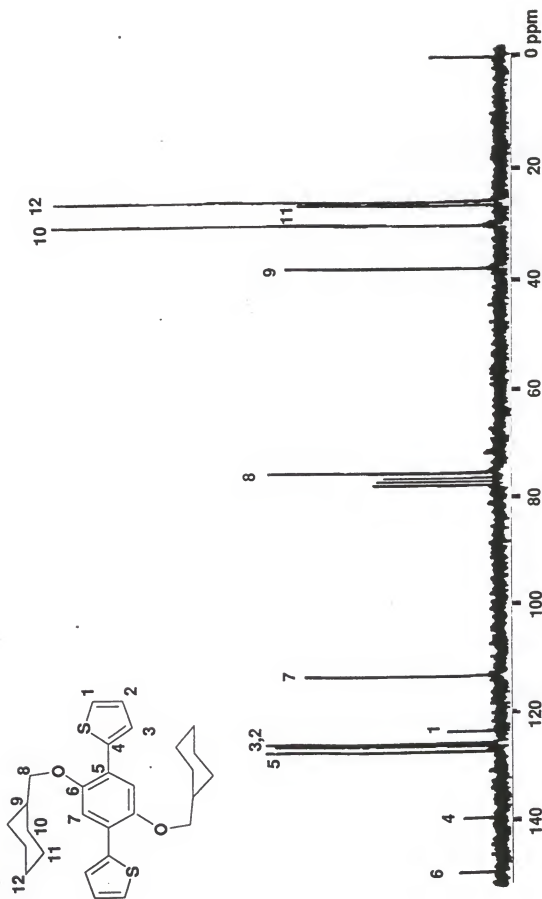
Figure. 2-3: ^{13}CNMR of 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene
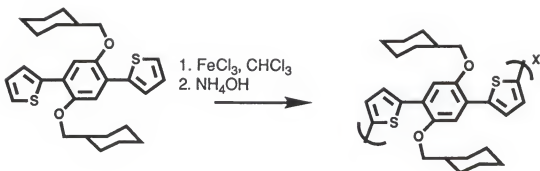
Figure. 2-4: Chemical polymerization of BTCMB

totally insoluble as shown in Figure 2-4. As illustrated in Figure 2-5, FTIR studies indicated the disappearance of the α C-H stretching of the thiophene moiety with the retention of the β C-H stretching as expected for the formation of a conjugated thiophene derivatized polymer.
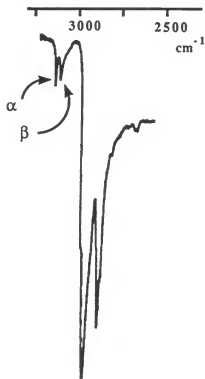
Figure. 2-5a: IR spectra of BTCMB
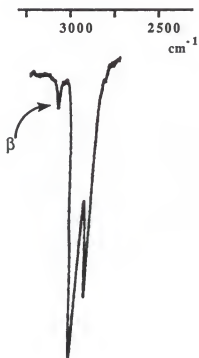
Figure. 2-5b: IR spectra of PBTCMB

TGA showed the polymer to be stable to ca. 300 °C (Figure. 2-6) and was amorphous as determined by X-ray diffraction. Elemental analyses showed that the product is relatively impure and difficult to purify due to its insolubility. While it is evident that BTCMB polymerizes under these oxidative conditions, this insolubility precluded proper structural analysis and study of electroactivity. Electrochemical methods were subsequently employed to probe polymerization and characterization of BTCMB.

2-3. Electrochemical Studies of BTCMB and PBTCMP

2-3-1. Electropolymerization of BTCMB

The monomer, BTCMB can be oxidatively polymerized using electrochemical methods to yield electrically conducting polymers. The electropolymerization and optoelectrochemistry was performed by Fernando Larmat. Electropolymerization was carried out using 10 mM monomer solution in 0.1 M TBAP/CH_3CN with platinum button electrode as working, platinum plate as counter and Ag/Ag$^+$ as reference electrodes. The polymer was deposited by scanning from 0.0 V to 1.2 V as shown in Figure 2.6. During anodic scanning of a monomer solution, a large irreversible current response indicates the formation and coupling of cation-radicals. The increased electron donating ability of the alkoxy groups results in a reduction of the monomer oxidation potential compared to the alkyl substituted monomers. Cyclic voltammetric scanning electropolymerization of bis(2-heterocycle)benzene (BHB) monomers is generally characterized by the observation of polymer cathodic processes during the reverse scan. Multiple scans to, or slightly beyond, $E_{p,m}$ then yields CV's where both the anodic and cathodic polymer redox processes grow in at potentials significantly lower than $E_{p,m}$. In contrast
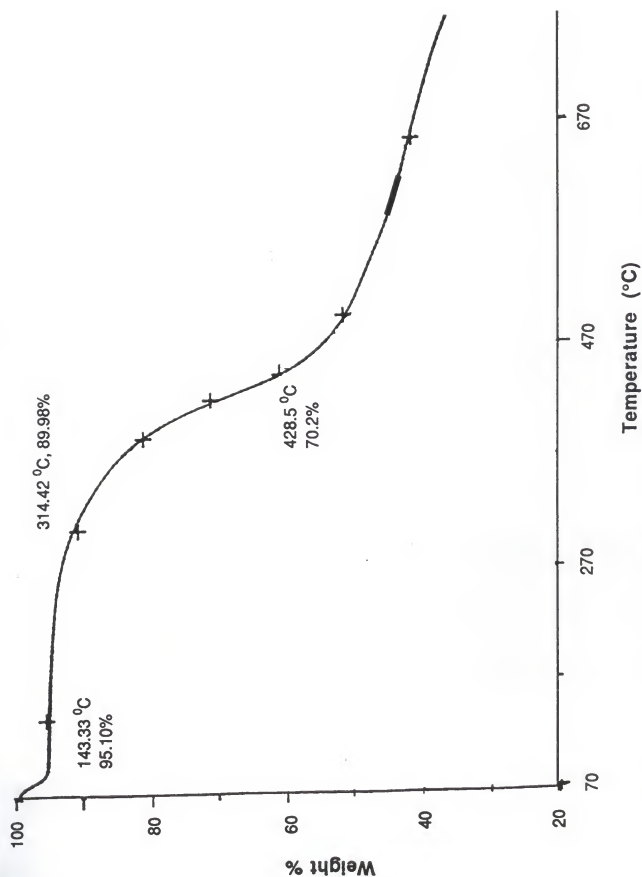
Figure. 2-6: TGA of poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene]
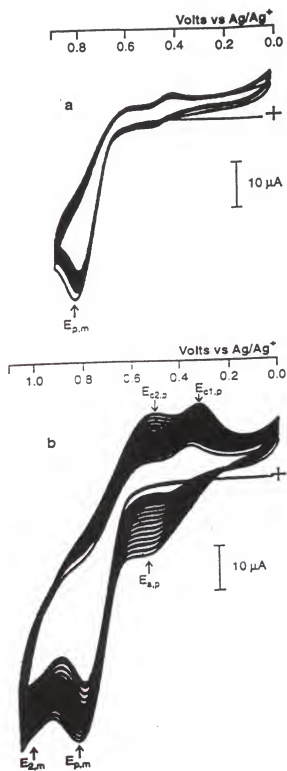
Figure. 2-7: (a) Slow film formation with scanning of BTCMB to E = +0.9V.
(b) Fast film formation with scanning to E = + 1.1V of BTCMB.

to all of the other substituted poly[1,4-bis(2-heterocycle)phenylenes] (PHBP's)
studied in our group, the cyclohexylmethyloxy substituted thiophene derivatives
(BTCMB) displays two monomer oxidation processes . Scanning to 0.9 V
(Figure 2-7a) results in an $E_{p,m}$ at 0.8 V. Repeated scanning, however, shows a
very slow film growth under these conditions. Extending the anodic scan to 1.1
V (Figure 2-7b) reveals a second oxidation ($E_{2,m}$) with an onset at 1.0 V.
repeated scanning under these conditions leads to the rapid development of
cathodic processes ($E_{c2,p}$ and $E_{c1,p}$) at 0.55 V and 0.35 V along with an anodic
process ($E_{a,p}$) at 0.5 V. During this excursion to higher potential, rapid
electroactive film growth is observed. This behavior may be due to the solubility
of oxidized oligomers formed at low potentials in the electrolyte, whereby newly
formed coupling products diffuse away from the electrode surface preventing
further coupling. This phenomenon was observed in other, highly soluble,
derivatives such as 1,4-bis(2-thienyl)-2,5-dodecyloxybenzene where the
solubility of the polymer precluded electrochemical polymerization.[79b] The
second oxidation of BTCMB results in rapid electroactive film deposition. It is
possible that this second process is due to the reaction of the coupled product
to form a new cation radical. Since the result of this oxidation is rapid coupling
resulting in the deposition of an insoluble film on the electrode surface, cross-
linking of the polymer is likely.

2-3-2. Electrochemical Quartz Crystal Microbalance (EQCM) Study of PBTCMP

To examine the potential dependence of this deposition further, the
electrochemical quartz crystal microbalance (EQCM), was used to monitor the
mass change during electropolymerization of BTCMB as shown in Figure 2-8.
Scanning to 0.9 V results in a frequency decrease (mass increase) as expected
for electropolymerization. During the return scan, the frequency increases as
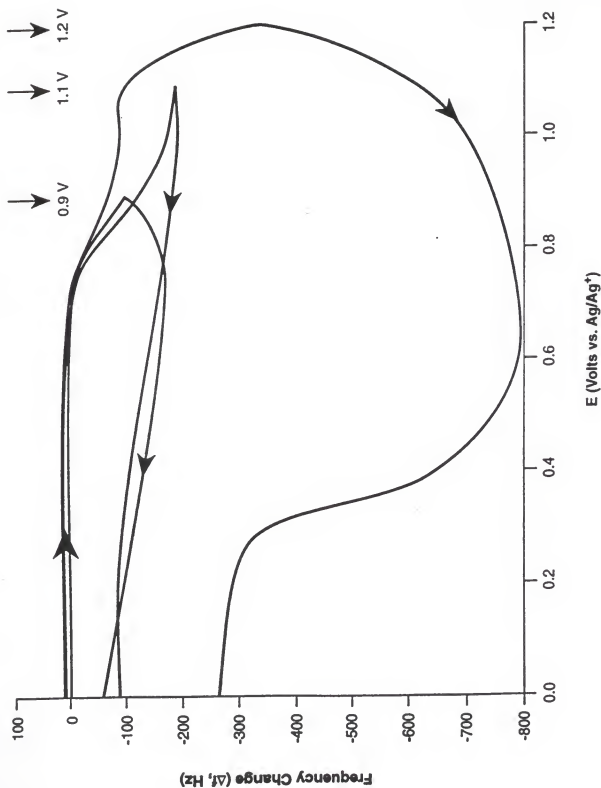
Figure. 2-8: EQCM monitored frequency shifts during deposition of poly[1,4-bis(2-thienyl)]-2,5-dicyclohexylmethyloxyphenylene] from 0.1M TBAP/CH₃CN at 0.9, 1.1 and 1.2 V.

the polymer formed dedopes and the anions are lost. A small net frequency change is observed at 0.0 V indicating a small amount of polymer has permanently adhered to the electrode surface during the initial scan. Scanning with a switching potential change of 1.1 V, a plateau is observed in the frequency change as the deposition occurs at a relatively slower rate on the electrode surface. Again the reverse scan shows a small irreversible mass change as a small amount of polymer deposition has occurred. Scanning beyond the second oxidation to 1.2 V results in a significantly large frequency decrease and rapid mass deposition as electroactive polymer forms on the working electrode. The return shows a frequency increase, again indicative of the expulsion of counterions during polymer reduction, but the large net mass increase at 0.0 V indicated a significant amount of polymer deposited during this scan.

2-3-3. Cyclic Voltammetry of Poly[1,4-bis(2-thienyl)-2,5-dicyclohexyl-methyloxyphenylene]

Films of PBTCMB were synthesized onto an Indium-tinoxide (ITO) coated glass electrode by repeated scanning of 10 mM BTCMB to +1.1 V in 0.1M TBAP/CH_3CN. The polymer was rinsed with CH_3CN and was used to study redox behavior in a monomer free 0.1M TBAP/CH_3CN system. PBTCMB was cycled at different scan rates between 0.0 and 0.8 V and the peak current response was measured. The increase in peak current response in directly proportional to the increase in the scan rate. The scan rate dependence is nearly linear in the range examined and indicates that the electroactive species is electrode bound. The decreased monomer oxidation potential of the alkoxy substituted monomer, in comparison with other alkyl substitutes BTHB's, leads to polymers with a lower degree of cross-linking and β-coupling. For example,
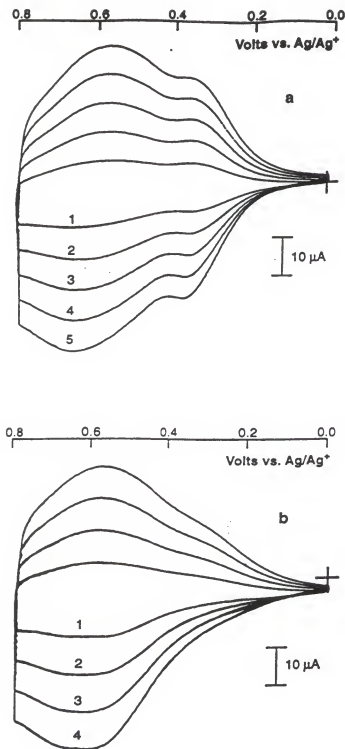
Figure. 2-9: CV of poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene] electrosynthesized by scanning to +1.1 V and switched in monomer-free 0.1 M TBAP in (a) CH_2Cl_2 and (b) CH_3CN as a function of scan rate.

the cyclic voltammogram of polythiophene electropolymerized from bithiophene displays two cathodic current responses, whereas the higher monomer oxidation potential of thiophene leads to films with a single redox couple.[84] The monomer, BTCMB, was polymerized at a potential beyond its initial monomer oxidation potential due to solubility concerns as described earlier. The cyclic voltammogram of its polymer lacks the first, low potential couple when cycled in CH_3CN, but displays two couples in a 0.1 M TBAP/CH_2Cl_2 system, as illustrated in Figure 2-9. All other linear alkoxy substituted polybisthienylphenylenes are soluble in CH_2Cl_2 indicating that it is a better solvent for these systems. This suggests that CH_2Cl_2 effectively swells the insoluble PBTCMP sufficiently to allow facile counterion insertion. These results suggest that the energy required for counterion insertion is an important factor in the stability of intermediate charge carriers.[84] The potential necessary to insert counterions into films of unsubstituted, alkyl substituted or crosslinked polymers is beyond the potential for bipolaron formation; therefore, a single two-electron oxidation results. The polymers which exhibit two couples allow facile counterion movement due to low oxidation potentials (resulting in minimal cross-linking during electropolymerization) and solvation effects induced by long side chains.

Two electrochemical properties support the suggestion that polarons are formed at the first redox couple of these polymers. First the peak widths of the first couple are quite small with respect to the second couple. Several polythiophene derviatives containing ether groups at the 3 position have been shown to display two distinct redox couples in their cyclic voltammograms, and the presence of a relatively sharp initial couple is characteristic of these systems.[82] The width of current responses in the cyclic voltammograms of surface bound species is ideally a constant value of 90.6/n mV where n is the number of electrons transferred. Larger values are indicative of repulsive

interactions within the film.[85] Because polarons possess only a single charge, and bipolarons contain two positive charges, repulsive interactions are expected to cause a larger peak broadening effect in the formation of bipolarons. The narrow current responses in the low potential couple of these system suggests that monovalent charge carriers rather that dicationic carriers are present.

Secondly, the peak separation of the second couple is significantly smaller in the polymers with two couples than in polymers which undergo a single, two-electron process. The large peak separation traditionally observed in conducting polymers has been ascribed to the large differences in conductivity between the oxidized and reduced states.[85] In those polymers where intermediate charge carriers are formed at a lower potential (polarons) the conductivity difference before and after the second oxidation is greatly reduced resulting in a near zero separation between the anodic and cathodic current responses.

2-3-4. Optoelectrochemistry of PBTCMP.

The electronic band structure of this polymer series has been investigated using optoelectrochemistry. The electronic band gap is determined from the onset of π to π^* transition. Poly[1,4-bis(2-thienyl)-2,5-dicyclohexyl-methyloxybenzene] was electrochemically synthesized on an ITO coated glass electrode at a constant potential of 1.1 V in 0.1M TBAP/CH_2Cl_2. The polymer's UV-Vis-NIR absorbance was measured *in situ* from 350 to 2500 nm as a function of applied potential as shown in Figure 2-10a. At 0.0 V, in its fully reduced state there is one strong absorbance with an onset at 2.4 eV and a peak at 2.75 eV due to the π to π^* transition of the neutral polymer. The potential was sequentially stepped anodically to oxidatively dope the polymer
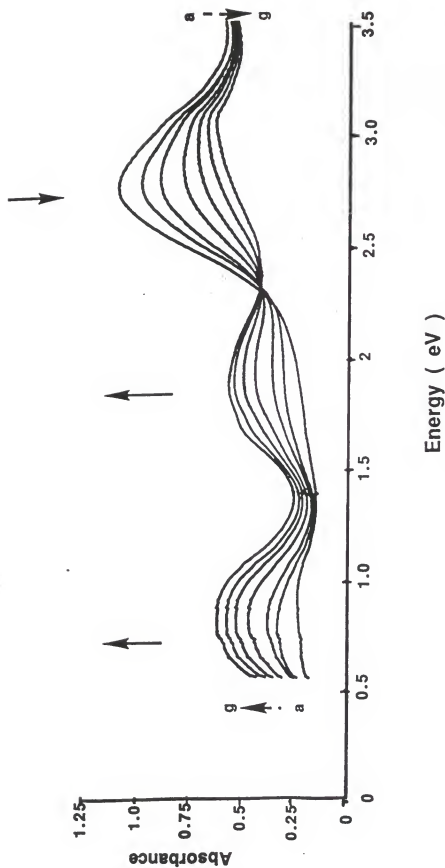
Figure. 2-10a: Potential dependence of the optical absorption for poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene] equilibrated in 0.1 M TBAP/CH₃CN at (a) 0.0 V, (b) 0.50 V, (c) 0.60 V, (d) 0.65 V, (e) 0.70 V, (f) 0.75 V and (g) 0.80 V.
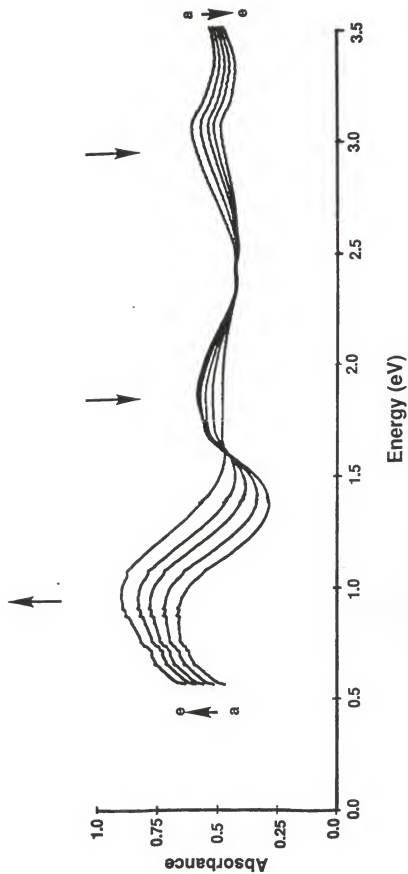
Figure. 2-10b: Potential dependence of the optical absorption for poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene] equilibrated in 0.1 M TBAP/CH₃CN at (a) 0.90 V, (b) 0.95 V, (c) 1.00 V, (d) 1.05 V and (e) 1.10 V.
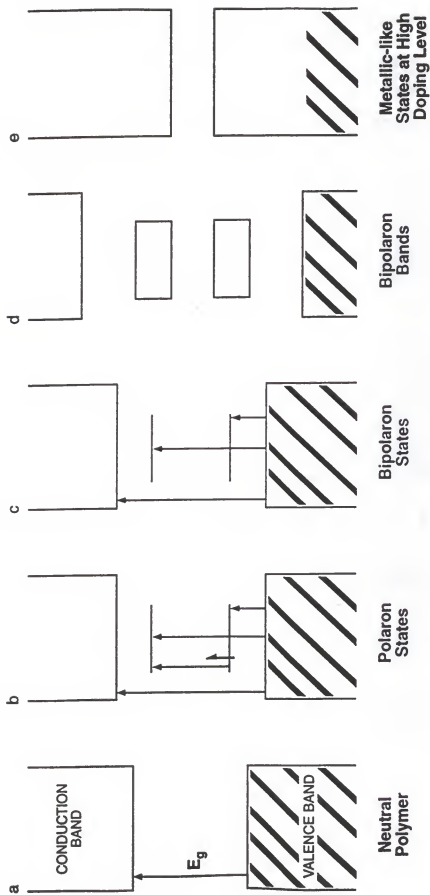
Figure. 2-11: The evolution of band structure at different doping levels of the poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene]

and a spectrum taken at a number of different oxidation states. As the potential is increased, two new absorbances at 1.45 eV and 0.55 eV are observed due to formation of bipolaron states leading to three different transitions. At the same time the intensity of the π to π^* transition decreases. As the potential is increased above 0.9 V, the intensity of absorption at 1.45 eV decreases while the other two absorption at 0.55 eV and 2.75 eV continue with their previous trend as illustrated in Figure 2-10b. At 1.1 V there is only one absorbance at 0.55 eV due to coalescence of bipolaron bands with the valence and conduction band.

The reduced PBTCMP has one transition for the band gap of the polymer. Upon electrochemical doping, there are new transitions observed due to the formation of bipolarons as explained in 1-8, and intragap electronic levels are created during charge carrier generation. As the doping levels is increased, the peak attributed to the transition between the valence band and the higher energy intragap state decreases in intensity, and the lowest energy transition shifts to shorter wavelengths. This change in the optical spectra can be attributed to the formation of metallic-like charge carriers.[86] The intragap bipolaron energy levels become sufficiently broad at high doping levels that they intersect with the valance and conduction bands as illustrated in the band structure diagram in Figure 2-11. This phenomenon has been observed previously in polythiophene derivatives but is conspicuously absent in other polyheterocylces.[86a] In our PBTP system, this behavior is observed in the alkoxy substituted derivatives.

2-4. EXPERIMENTAL

2-4-1. Materials and Methods.

Cycohexylmethylbromide, hydroquinone, bromine, KOH, thienyllithium, zinc chloride, palladium tetrakistriphenylphosphine were used as purchased from Aldrich without any further purification. All solvents were freshly dry distilled before use. All reactions were carried out under an argon atmosphere. Characterization was carried out using ^{1}H and ^{13}C NMR spectroscopy on Varian XL-200 and Varian XL-300 MHz spectrometers, FTIR on a Biorad/Digital FTS-40 spectrophotometer, and mass spectrometry on a Finnigan MAT 95 Q spectrometer. Elemental analysis was performed by Atlantic Microlab Inc.

2-4-2. Electrochemical and Spectroscopic Methods.

Cyclic voltammetry was conducted utilizing platinum working and counter electrodes and an Ag/Ag$^+$ reference electrode. Potentials were controlled using a PAR EG&G model 273 potentiostat/galvanostat. Polymer films for optoelectrochemical measurements were prepared on ITO coated glass slides (Delta Technologies) as the working electrode. Electrolytes employed were 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile or methylene chloride (distilled over P_2O_5 prior to use). Electronic spectra were obtained using a Varian Cary 5E UV-Vis-NIR spectrophotometer. Experimental details have been presented previously.[79d] Mass changes at gold working electrodes (Valpey-Fisher) were monitored using the electrochemical quartz crystal microbalance (EQCM) as described previously.[83]

2-4-3. Monomer Synthesis

2-4-3-1. 1,4-Dicyclohexylmethyloxybenzene (1-I)

Alcoholic KOH (14.5 g, 258 mmol) was added slowly to hydroquinone (13.5 g, 123 mmol) in 100 ml of ethanol. The reaction mixture was stirred for

two hours and 50 g, (282 mmol) of cyclohexylmethylbromide in 50 ml of ethanol was added drop-wise over a period of 30 minutes. The mixture was refluxed for 48 hours and the ethanol was distilled. The residue was extracted with CCl_4, dried over $CaCl_2$ and filtered. The solution was evaporated to dryness and white flaky crystals were obtained after recrystallization from ethanol. ^1H NMR (ppm): 6.85(s), 3.7(d, $J = 7.7$ hz) 1-2(m). ^{13}C NMR (ppm): 154.9, 116.9, 75.9, 39.2, 31.4, 28.2, 27.1. (mp = 93-95 ^{o}C, (23 g) 64 %). HRMS: molecular ion peak, 302.2239 amu (theoretical 302.4558); base peak, 206.1242 amu.

2-4-3-2. 1,4-Dibromo-2,5-dicyclohexylmethyloxybenzene.(1-II)

Bromine (12 g; 76 mmol), in 100 ml of CCl_4 was added drop-wise to a 150 ml CCl_4 solution of **1-1** (7.6 g; 25 mmol). The reaction mixture was stirred for 72 hours, poured in 150 ml of 1.0 M KOH and stirred for 2 additional hours. The aqueous layer was discarded and the organic layer washed with dilute HCl until the pH became 7.0. The solution was concentrated by evaporation and poured slowly into cold methanol. The precipitate was collected by filtration, dried and recrystallized from ethyl acetate to give 10.2 g of white solid. (mp = 130-132 ^{o}C, 89%). ^1H NMR (ppm): 7.05(s) 3.73(d, $J = 7.5$ hz) 1-2(m). ^{13}C NMR (ppm): 150.2, 111.4, 111.1, 75.6, 37.7, 29.8, 26.5, 25.8. Anal. Calcd. for $C_{20}H_{28}O_2Br_2$: C, 52.19; H, 6.13. Found: C, 51.95; H, 6.13.

2-4-3-3. 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene (1-III).

2-Thienyl lithium (36 mmol) was added slowly with stirring at $0^{o}C$ to a flask containing zinc chloride (8.7g; 64 mmol) in 100 ml of THF. In a separate flask, the dibromide (**1-II**) (5.5g; 12 mmol), in 100 ml of THF was added to 50 mg of palladium tetrakistriphenylphosphine via cannula at 0 ^{o}C over a period of 30 min. The 2-thienylzinc chloride was cannulated into the flask containing **1-II** and the mixture was stirred for 72 hours. The mixture was then poured into 100 ml of dilute HCl and the organic layer was separated. The aqueous layer was

extracted with ether and the ether fractions were combined. The product was precipitated in cold methanol and recrystallized from acetone to yield 4.6g of greenish solid. (mp = 162-164 °C, 82%). ^{1}H NMR (ppm): 7.52(dd, J = 3.6, 1.2 hz), 7.33(dd, J = 5.2, 1.2 hz), 7.11(dd, J = 3.8, 1.6 hz), 3.8(d, J = 5.8 hz), 1-2(m). ^{13}C NMR (ppm): 149.3, 139.3, 126.6, 125.6, 125.1, 122.9, 112.8, 75.3, 37.9, 30.1, 26.5, 25.9. Anal. Calcd. for $C_{28}H_{34}O_2S_2$ C, 72.06; H,7.34; S,13.74. Found: C, 71.98; H,7.42; S,13.56. HRMS: molecular ion peak, 466.2019 amu; base peak, 274.0139 amu.

2-4-4. Poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene].

Ferric chloride (140 mg, 0.851 mmol) and 200 ml of CHCl$_3$ were refluxed for 2 hours and cooled. The monomer, **1-III**, (100 mg, 0.214 mmol) was added with 75 ml of CHCl$_3$. The mixture was refluxed for 72 hours. The solvent was removed by rotovap and the product re-precipitated in cold methanol. The black-red powder was compensated by the addition of 30 ml of concentrated ammonium hydroxide to yield the brick red neutral polymer. Anal. Calcd. for $C_{28}H_{32}O_2S_2$: C, 72.06; H, 7.34; S, 13.74. Found: C, 71.98; H, 7.4; S, 13.56.

ELECTROCHEMISTRY, ELECTROCHROMISM AND LONG TERM SWITCHING
STABILITY OF POLY(3,4-ETHYLENEDIOXYTHOPHENE) AND ITS ALKYL
DERIVATIVES

3-1 Introduction

It is important to synthesize electroactive and conducting polymers
having low oxidation potentials which yield materials of high ambient stability in
the conducting state.[87] Of the conducting polymers studied, polypyrrole[88] and
polyaniline[89] stand out for their ease of oxidation and stability making them the
materials of choice for applications and commercial consideration. Among the
conjugated heterocyclic polymers that have been studied extensively,
polythiophenes have attracted attention due to their ease of derivatization and
polymerizability by chemical and electrochemical methods.[90]

Unsubstituted polythiophenes are insoluble and infusible. Alkyl chain
derivatization at the 3-position induces solubility and fusibility into the polymers,
making them true thermoplastics.[91] Attachment of an electron donating alkoxy
group to the 3-position of the thiophene reduces the polymer's oxidation
potential yielding better electrical and optoelectronic properties.[92] This electron
donating group raises the highest occupied molecular orbitals (HOMO), thereby
lowering the oxidation potential, while having less effect on the lowest
unoccupied molecular orbitals (LUMO), which decreases the polymer's
electronic band gap.[93] Disubstitution at the 3 and 4 positions, which would
eliminate the possibility of β coupling and crosslinking, leads to strong steric

interactions along the chains reducing conjugation.[94] One method of overcoming these steric interactions is to fuse a cyclic ring on to the thiophene.

Poly(ethylenedioxythiophene) (PEDOT, R=H) has a dioxane ring fused on to the *c* face of the thiophene. This cyclic substituent presents less steric demands than those encountered with a disubstituted polythiophene. PEDOT has a lower oxidation potential than any of the polythiophenes reported,[95] making it quite stable under ambient conditions and potentially useful in many applications as an anti-static material[96] and as a solid electrolyte in capacitors.[97] Thin films of the polymer are light blue-gray in their oxidized state and dark blue-violet in their reduced state.[98] This optical contrast between the oxidized and reduced states forebodes the use of PEDOT as an electrochromic material.[99]

In order to develop new electrochromic polymers, and to understand substituent effects, octyl and tetradecyl substituted poly(ethylenedioxy-thiophenes) (PEDOT-C_8 and PEDOT-C_{14}) were synthesized. This chapter outlines the structure-property relationships in these polymers and compares them to the parent PEDOT.

3-2 Synthesis

3-2-1 Ethylenedioxythiophene and its alkyl derivatives

The EDOT monomers were synthesized by modifying methods first reported by Fager.[100] Thiodiglycollic acid was esterified with ethanol in the presence of an acid catalyst to yield the ester, diethylthioglycollate (**3-1**) as shown in Figure 3-1. This diester was reacted with diethyloxalate in the presence of sodium ethoxide to obtain the ring closed thiophene moiety, disodium salt of 2,5-dicarboethoxythiophene-3,4-dioxide (**3-2**). The disodium
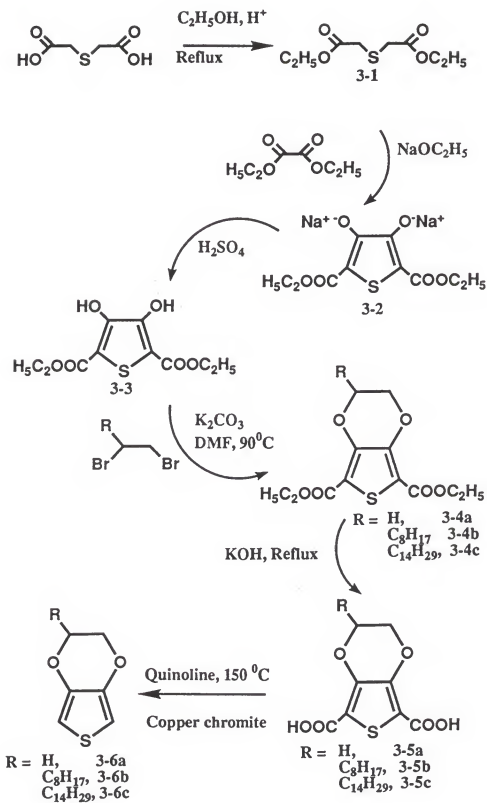
Figure 3-1: Schematic diagram for synthesis of EDOT monomers

salt was acidified to yield 3,4-dihydroxy-2,5-dicarboethoxythiophene (**3-3**). The diol was reacted with 1,2-dibromoalkane (prepared from bromine and the required alkene) in anhydrous DMF to yield the alkyl substituted (octyl and tetradecyl) 2,5-dicarboethoxy-3,4-dioxyethylenethiophenes (**3-4b** and **3-4c**). This ring closed diester thiophene moiety was hydrolyzed with KOH resulting in the formation of diacids (**3-5b** and **3-5c**) which were subsequently decarboxylated in quinoline with copper chromite as a catalyst to yield the monomers, 5-octyldioxeno[2,3-c]thiophene (**3-6b**, EDOT-C$_8$) and 5-tetradecyldioxeno[2,3-c]thiophene (**3-6c**, EDOT-C$_{14}$). The unsubstituted derivative, EDOT is now commercially availabe at Bayer.

3-2-2 Characterization of monomers, EDOT and its octyl (EDOT-C$_8$) and tetradecyl (EDOT-C$_{14}$) derivatives

^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis were used to characterize the monomers. The proton NMR spectra for both the EDOT-C$_8$ and EDOT-C$_{14}$ shows four different sets of peaks shown in Figures 3-2 and 3-3. The methyl and methylene proton peaks of the alkyl chains can be observed at 0.9 and between 1.2 to 1.7 ppm; the methine and methylene peaks of the ethylenedioxy segment between 3.8 and 4.2 ppm as an ABX pattern; and the aromatic protons of the thiophene rings can be seen at 6.3 ppm. The area under these peaks integrate to the required number of protons of the molecules within the specific regions. The ^{13}C NMR spectra for the monomers are shown in Figures 3-4 and 3-5. Resonances are observed between 15 and 35 ppm for the alkyl cabon atoms; 75 and 68 ppm for the methine and methylene carbons of the ethylenedioxy segment; and 112 and 142 ppm for the aromatic carbon atoms of the thiophene moiety of the monomers. The mass spectrometry and
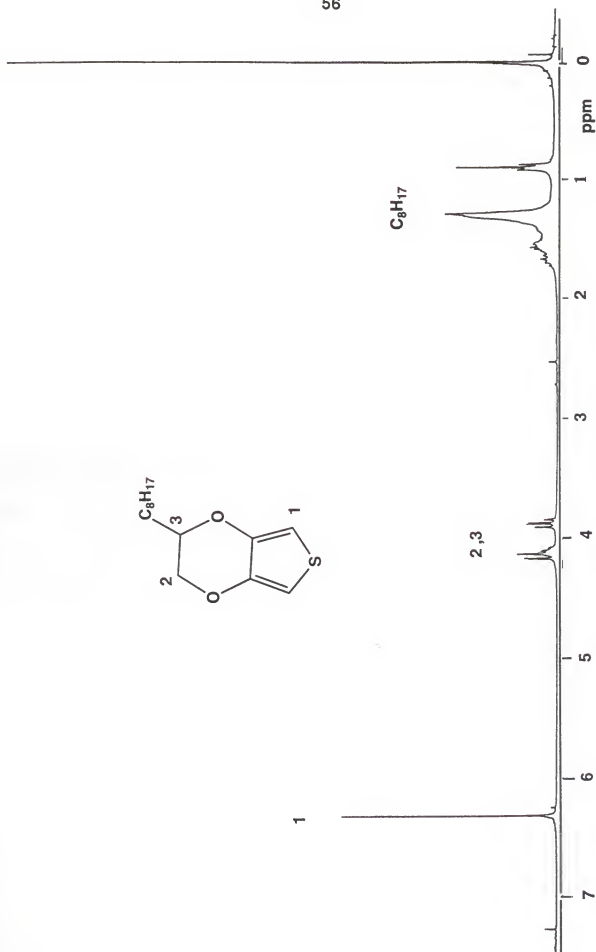
Figure 3-2: ^{1}H spectra of EDOT-C$_8$
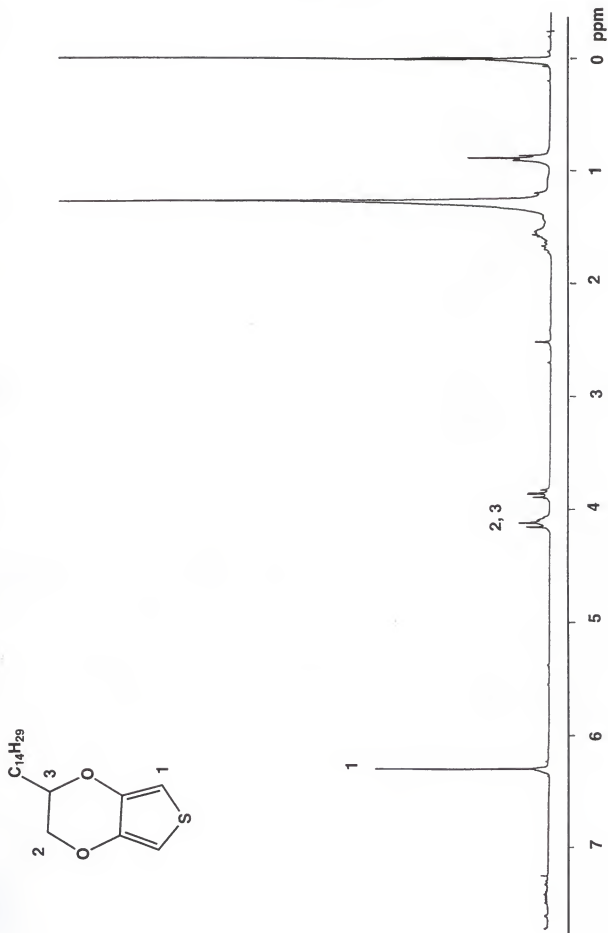
Figure 3-3: ^{1}H spectra of EDOT-C$_{14}$
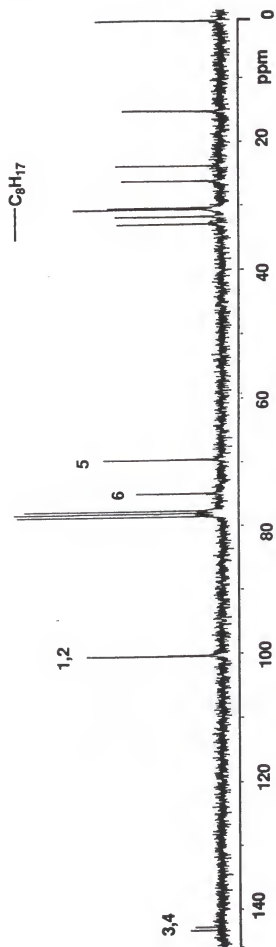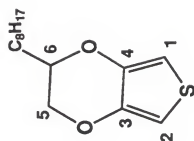
Figure 3-4: ^{13}C spectra of EDOT-C_8
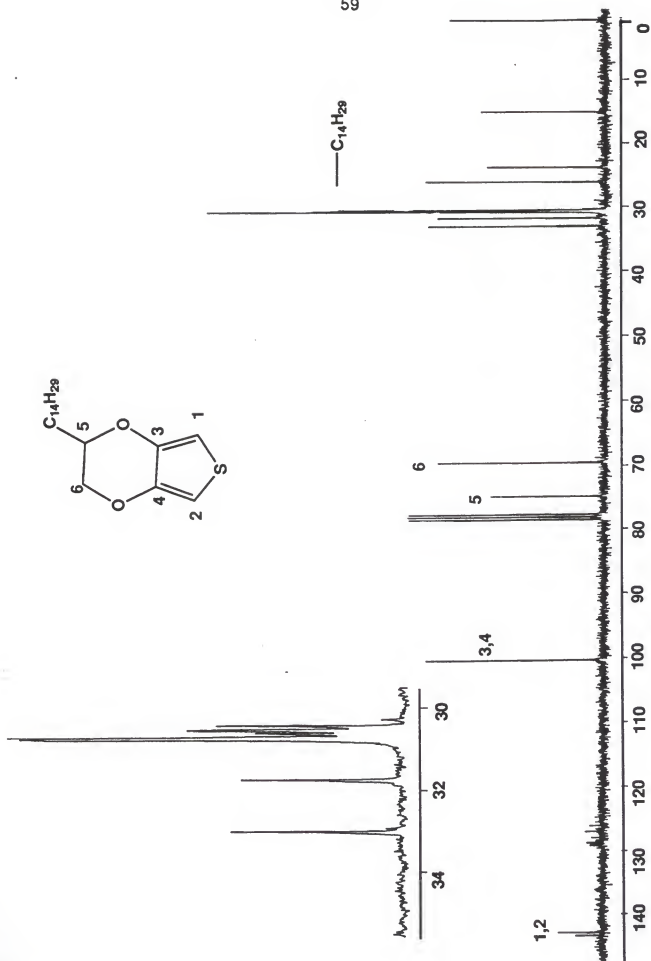
Figure 3-5: ^{13}C spectra of EDOT-C_{14}

elemental analysis results of these monomers show the expected values further confirming the structure of the molecule.

3-3 Electrochemisry of EDOT and its alkyl derivatives

3-3-1 Electrochemical Polymerization

EDOT-C_8 and EDOT-C_{14} were electrochemically polymerized in a number of solvent/electrolyte combinations. A general electropolymerization path is outlined in Figure 3-6. The parent monomer, EDOT, exhibits a monomer oxidation peak ($E_{p,m}$) at 1.0 V while EDOT-C_8 and EDOT-C_{14} exhibit $E_{p,m}$'s at 0.89 V and 0.92 V respectively in 0.1 M TBAP/CH_3CN as illustrated in Figure 3-7. During this oxidation, the monomers polymerize and electroactive polymer films grow on the working electrode surface. On the reverse scan of the CV's, EDOT-C_8 exhibits two cathodic peaks at -0.14 ($E_{c2,p}$) and -0.52 V ($E_{c1,p}$), while EDOT-C_{14} exhibits two similar peaks at -0.14 V ($E_{c1,p}$) and -0.32 V ($E_{c2,p}$), which can be attributed to reduction of the oxidized polymer. The PEDOT-C_8 formed re-oxidizes at -0.22V ($E_{a,p}$), while the PEDOT-C_{14} formed re-oxidizes at -0.19 V ($E_{a,p}$). As the electropolymerization of these monomers is continued by repeated scanning, the oxidation and reduction peak currents increase and shift slightly in potential. This increased current is due to build-up of the electroactive polymer on the electrode.

The polymer deposited onto the electrode is then cycled in a monomer free electrolyte to study its stability and reversibility of its redox behavior. All three polymers are well behaved and reversibly redox switch. This is illustrated in Figure 3-8 for PEDOT-C_{14} grown and switched in 0.1M TBAP/CH_2Cl_2. Analysis of the cyclic voltammetric behavior of the polymers in monomer free electrolyte show all of the peak currents scale linearly with the scan rate,
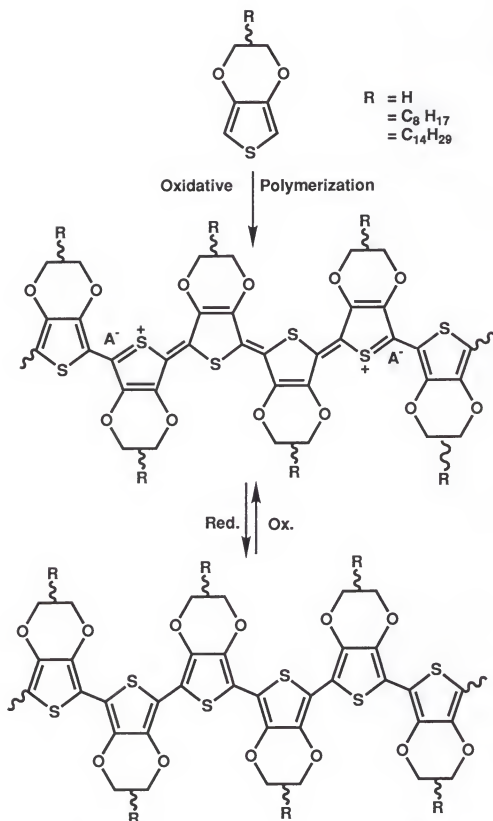
Figure 3-6: Oxidative polymerization and polymer redox reaction for EDOT and its alkyl derivatives

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Cyclic Voltammetric Growth of PEDOT-C$_8$

Cyclic Voltammetric Growth of PEDOT-C$_{14}$

Volts vs Ag/Ag$^+$

$E_{c2,p}=-0.55$

$E_{a,p}=-0.22$

$E_{c1,p}=0.18$

$E_{a,m}=0.89$

$E_{c2,p}=-0.36$

$E_{a,p}=0.19$

$E_{c1,p}=0.16$

$E_{a,m}=0.93$

5 µA

50 µA
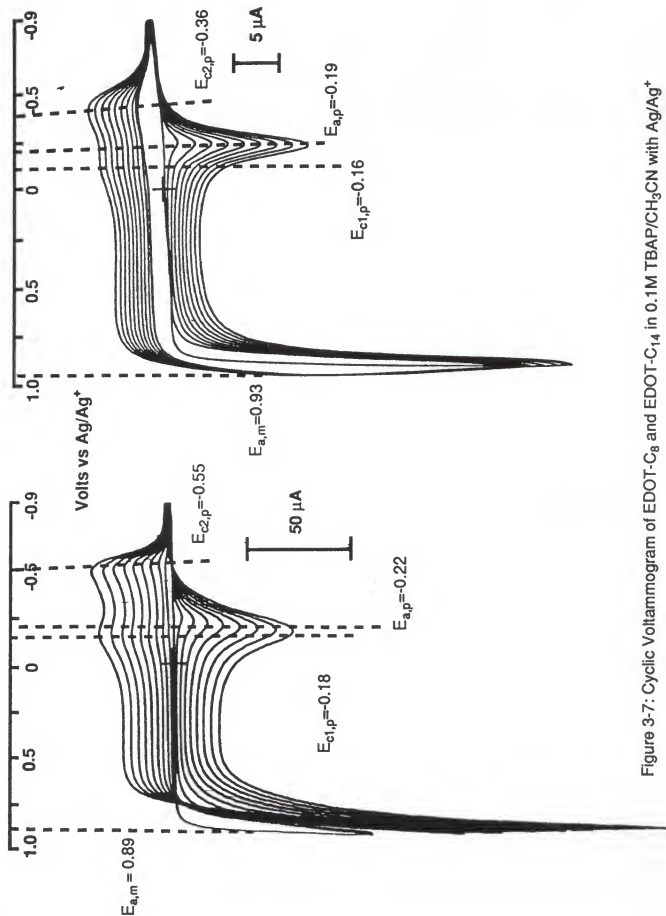
Figure 3-7: Cyclic Voltammogram of EDOT-C$_8$ and EDOT-C$_{14}$ in 0.1M TBAP/CH$_3$CN with Ag/Ag$^+$
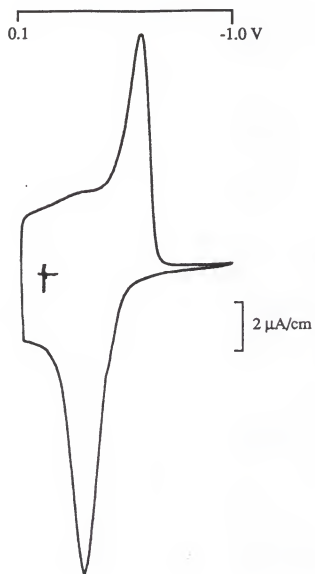
Figure 3-8: Cyclic voltammogram of PEDOT-C$_{14}$ at 100mV/sec in 0.1MTBAP/CH$_2$Cl$_2$ vs Ag/Ag$^+$

indicating that the polymer (and thus all electroactive sites) is adhered to the surface of the electrode as seen in Figure 3-9a.

3-3-2 Solvent and Electrolyte Dependence of Electropolymerization.

EDOT-C_8 and EDOT-C_{14} were polymerized by the repeated scanning methodology onto ITO coated glass in a series of solvent/electrolyte systems and their electrochemical properties during film growth compared as shown in Table 1. Both PEDOT-C_8 and PEDOT-C_{14} show two redox processes upon reduction in 0.1 M LiClO$_4$/CH$_3$CN, and 0.1 M TBAP/CH$_3$CN. Figure 3.9b illustrates the two redox processess during the reduction of PEDOT-C_8 in 0.1 M TBAP/CH$_3$CN. The polymers deposited in CH$_3$CN show a well behaved redox behavior. The two redox processess during reduction are due to the transformation of the oxidized polymer to radical cation and then to final reduced form. In 0.1 M LiClO$_4$/PC and 0.1 M TBAP/CH$_2$Cl$_2$ there is only one broad redox response during reduction. The radical cation formed in PC and CH$_2$Cl$_2$ is not discernible. 0.1 M LiClO$_4$/Tetraglyme was utilized as a potential electrochemical medium, but did not allow for the deposition of electroactive polymer. The polymers formed are soluble in tetraglyme, making it impossible to grow a film.

The amount of electroactive polymer deposited with repeated scanning was compared for EDOT, EDOT-C8 and EDOT-C14 as a function of electrodeposition medium. The anodic current response for the polymer oxidation on the tenth scan during deposition was monitored as a means of determining the relative amounts of polymer deposited as shown in Table 2. It can be seen that the electrodeposition rate of EDOT proceeds more rapidly than EDOT-C8, which is more rapid than EDOT-C14 in all of the solvent/electrolyte systems studied. This can be attributed to solubilization of the oligomers
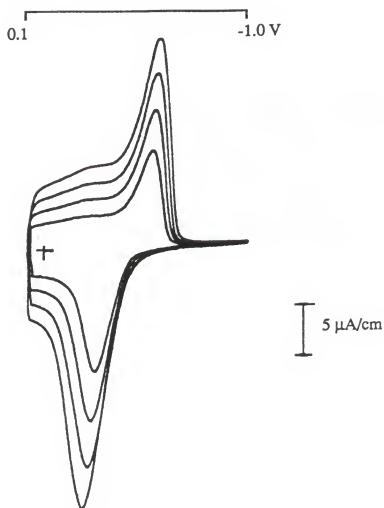
Figure 3-9a: Scan rate dependence of PEDOT-C$_{14}$ in 0.1 M TBAP/CH$_2$Cl$_2$ at 100, 150, 200 and 250 mV/sec.
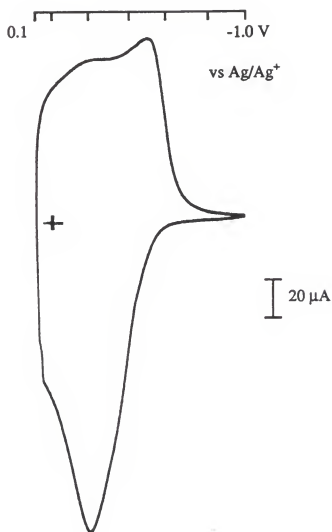
Figure 3-9b: Cyclic voltammogram of PEDOT-C8 in 0.1 M TBAP/CH3CN showing
two redox processes during reduction.

Table 1. Electrochemical Potentials[a] for Monomer Oxidation and Polymer Redox Electroactivity

Polymerization	EDOT-C$_8$				EDOT-C$_{14}$			
Electrolyte System	$E_{p,m}$	$E_{a,p}$	$E_{c1,p}$	$E_{c2,p}$	$E_{p,m}$	$E_{a,p}$	$E_{c1,p}$	$E_{c2,p}$
0.1 M TBAP / CH$_3$CN	0.89	-0.22	-0.14	-0.52	0.92	-0.19	-0.14	-0.32
0.1 M TBAP / CH$_2$Cl$_2$	0.96	-0.24		- 0.56	0.96	-0.22		- 0.54
0.1 M LiClO$_4$ / PC	1.01	0.05		- 0.3	0.78	-0.15		- 0.2
0.1 M LiClO$_4$ / Tetraglyme	No polymer was deposited on the electrode surface, as the oligomers dissolved							
0.1 M LiClO$_4$ / CH$_3$CN	1.0	-0.2	-0.2	-0.5	0.96	-0.1	-0.2	-0.44

[a] Volts versus Ag / Ag$^+$ (0.01M) reference electrode.

Table 2. Solvent/Electrolyte Dependence of Polymer Redox Electroactivity

Redox Switching	Peak Anodic Current Response (μA)[a]		
Electrolyte System	PEDOT	PEDOT-C_8	PEDOT-C_{14}
0.1 M LiClO$_4$/CH$_3$CN	235	162	64
0.1 M TBAP/CH$_3$CN	115	84.6	33.8
0.1 M LiClO$_4$/PC	46	42	22
0.1 M TBAP/CH$_2$Cl$_2$	38	20	14.4

[a] Cyclic Voltammograms run at 100 mV/s on polymer films deposited during 10 cyclic scans between - 0.8 V to 1.0 V in 10 mM of monomer solution of the same solvent/electrolyte combination.

forming at the electrode surface by the long alkyl chains. Comparing solvents, it can be seen that the deposition is most efficient in CH_3CN based electrolytes and least efficient in CH_2Cl_2. This is due to the fact that CH_2Cl_2 is a better solvent for thiophene based polymers. In a practical sense, 0.1 M $LiClO_4$ / CH_3CN serves as the best electrodeposition medium for EDOT and alkyl substituted EDOT polymers.

3-3-3 Optoelectrochemical Analyses

In order to probe the electronic structure of the polymers, and to examine the optical changes that occur during redox switching, which are important for electrochromic applications, optoelectrochemical analyses were carried out. A film of the unsubstituted parent polymer, PEDOT, was potentiostatically synthesized from 10mM EDOT and 0.1 M $LiClO_4/CH_3CN$ solution on an ITO coated glass electrode at 1.1 V. After rinsing the film with monomer free electrolyte, the polymer coated ITO glass electrode was used as the working electrode, along with Ag/Ag^+ (0.01 M) as reference and platinum as counter electrodes in 0.1 M $LiClO_4/CH_3CN$. The optoelectrochemical spectral series was monitored while scanning from 300 nm (4.1 eV) to 1600 nm (0.78 eV) as the polymer was sequentially stepped between -1.0 V and 0.6 V as shown in Figure 3-10. When held at a reducing potential of -1.0 V, PEDOT exhibits an E_g of approximately 1.6-1.7 eV and has a strong absorbance peak at 2.2 eV causing the films to be deep blue and absorbing. As the potential was sequentially increased, this peak reduces in intensity , with the concommitant growth of a low energy absorption at 1.4 eV. In the highly oxidized state, a contiuous absorption band through the NIR is observed which tails into the visible region of the spectrum, leaving the film in a sky blue and transmissive state. Figure 3-11 shows the optoelectrochemical series for a PEDOT-C_{14} film

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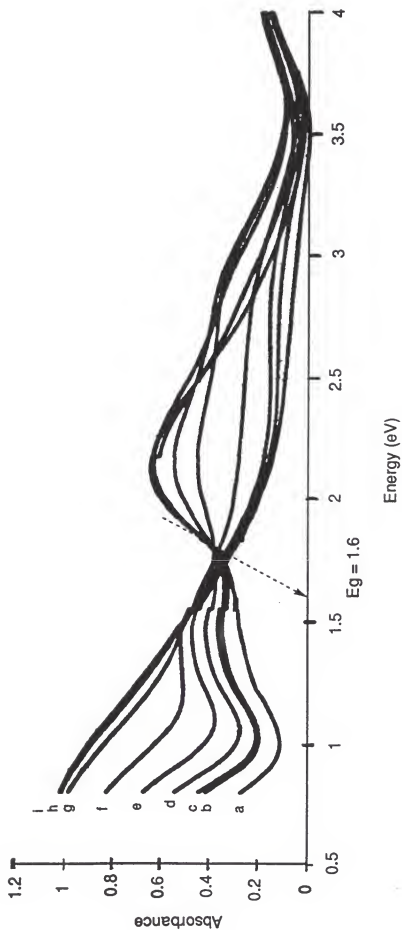
Figure 3-10: Optoelectrochemical studies of PEDOT in 0.1M LiClO$_4$/CH$_3$CN at a = -1.0, b = -0.8, c = -0.6, d = -0.4, e = -0.2, f = 0.0, g = 0.2, h = 0.4, i = 0.6 V vs Ag/Ag$^+$
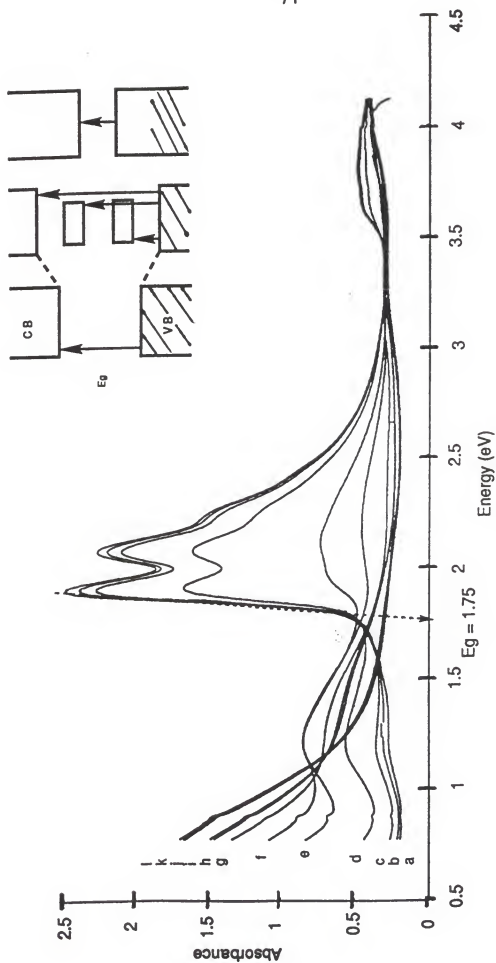
Figure 3-11: Optoelectrochemical studies of PEDOT-C$_{14}$ in 0.1M LiClO$_4$/CH$_3$CN at a = -0.8, b = -0.6, c = -0.4, d = -0.3, e = -0.2, f = -0.1, g = 0.0, h = 0.2, i = 0.4, j = 0.6, k = 0.8, l = 1.0.

synthesized using the methodology described for PEDOT at a constant potential of 1.0 V. The absorbance was monitored *in situ* as a function of potential between -0.8 V and 1.0 V. In the reduced, neutral, form the polymer exhibits a high absorbance throughout the visible region (1.75 eV to 3.0 eV) and is a deep purple in color. As the potential is increased, the visible absorbance decreases to the point that the film is light gray and quite transmissive when oxidized. Similar behavior is found for PEDOT-C_8 as seen in Figure 3-12. The E_g values of both PEDOT-C_8 and PEDOT-C_{14} are approximately 1.75 eV. The Eg values for the polymer does not vary as the elelctrolyte or solvent is changed. Comparison of Figure 3-10 with Figures 3-11 and 3-12 bring out the important similarities and differences of the substituted and non-substituted polymers. In the neutral state, PEDOT exhibits a single broad absorption, while the interband transition for PEDOT-C_{14} (and PEDOT-C_8) is split into two peaks at 1.9 eV and 2.1 eV along with a high energy shoulder at 2.2 eV. This splitting can be attributed to the vibronic coupling with the electronic absorption.[101]

Both PEDOT, PEDOT-C_8 and PEDOT-C_{14} lose absorption throughout the visible region due to depletion of the interband transition, while concurrently increasing absorption in the NIR region with doping due to formation of bipolaronic bands. PEDOT exhibits an increase of NIR absorption with a peak evolving at 1.4 eV along with a low energy absorbance below 1 eV. In the case of PEDOT-C_8 and PEDOT-C_{14}, a peak evolves at 1.25 eV. Above 0.0 V the peak at 1.25 eV starts to decrease in intensity as absorption continues to increase at 0.8 eV. At the highest oxidation levels the inter-band transition and the transistion at 1.25 eV reach a minimum, while the absorbance at 0.8 eV continues to grow leading to a second isobestic point at 1.1 eV. This causes PEDOT-C_8 and PEDOT-C_{14} to have a lower absorption throughout the visible region compared to unsubstituted PEDOT. This high optical contrast in the
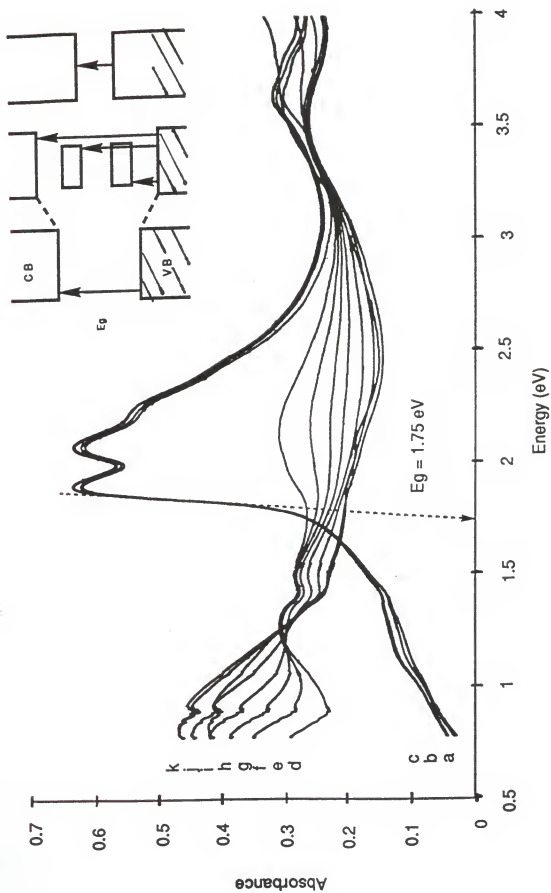
Figure 3-12: Optoelectrochemical studies of PEDOT-C$_8$ in 0.1M TBAP/CH$_3$CN at a = -1.0, b = -0.8, c = -0.6, d = -0.4, e = -0.2, f = -0.1, g = 0.0, h = 0.1, i = 0.3, j = 0.5, k = 0.8.

visible region for the substituted polymers, make them better materials for electrochromic devices. At high potentials the bipolaronic bands coalesce with the valence and conduction bands giving rise to only a single absorption at low energy suggesting metallic-like state at this potentials.[86]

The optoelectrochemical spectral series for PEDOT-C_{14} was examined using two further electrolyte/solvent systems for growth and switching (0.1 M LiClO$_4$/PC and 0.1 M TBAP/CH$_3$CN). In both cases, essentially identical band gaps, energies of transitions, existence and energies of isosbestic points were found. The major difference was the overall absorbance values, though each film was deposited with an identical amount of charge (100 mC/cm^2). The absorbance at λ_{max} (ca. 1.9-2.0 eV) for the neutral polymer was found to 2.4, 1.7 and 0.8 for films synthesized and switched in LiClO$_4$/CH$_3$CN, TBAP/CH$_3$CN, and LiClO$_4$/PC respectively. This scales with the polymer's anodic current response results reported in Table 2 and serves as a confirmation of the solvent/electrolyte dependence for the efficiency of electropolymerization.

3-4 Long Term Switching Studies

3-4-1 Switching under ambient conditions

Long term switching studies were carried out to monitor absorbance changes with time during repeated potential stepping between reduced and oxidized states to obtain an insight into changes in the optical contrast. As shown in Figure 3-13a and 3-13b, unsubstituted PEDOT was switched by stepping the potential between -1.1 V to + 1.1 V with a switching interval of 20 seconds in a 0.1 M TBAP/CH$_3$CN electrolyte. The polymer film changed from a dark blue absorptive reduced state at -1.1 V to a light gray transmissive oxidized state at +1.1 V with a high contrast. This switching could be carried out a

Figure 3-13a: Long term switching studies of PEDOT in 0.1M TBAP/CH$_3$CN. (Switches 1-3 shown).
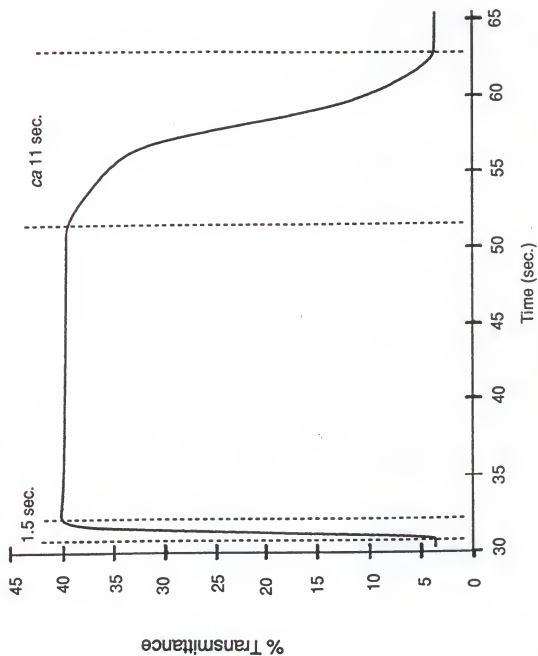
Figure 3-13b: Optical transmittance PEDOT in 0.1M TBAP/CH$_3$CN for the 3 rd switch

Figure 3-14a: Long term switching studies of PEDOT-C$_{14}$ in 0.1M TBAP/CH$_3$CN. (Switches 16-21 shown).
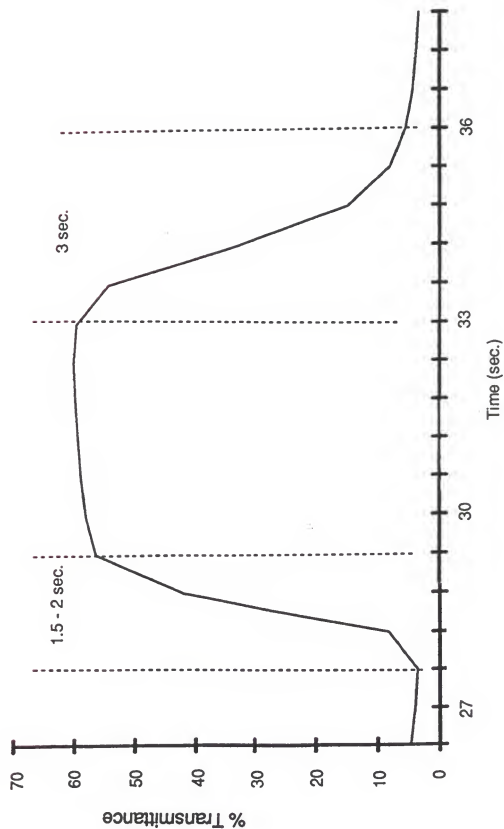
Figure 3-14b: Optical transmittane of PEDOT - C_{14} in 0.1M TBAP/CH$_3$CN for the 19th switch

number of times with little loss of optical contrast. It can be seen that the reductive process proceeds significantly more rapidly than the oxidation process. While the reduction is complete in *ca.* 1.5 seconds, reoxidation requires greater than 10 seconds. As the film is oxidized, the polymer layer in contact with the electrode oxidizes initially and a conductive front propagates through the polymer. The rapidity of the oxidation can be attributed to the ease of transport through the conducting film from the electrode contact. The reduction of the oxidized film forms an insulator at the polymer-electrode interface, leading to longer time for complete reduction of the film.

It was found that the alkyl substituted polymers are significantly faster in their redox switching rates than the unsubstituted derivative. For example, Figure 3-14a and 3-14b shows the switching of PEDOT-C_{14} between -0.8 V and 0.6V with a switching interval of 5 seconds in 0.1 M TBAP/CH_3CN. PEDOT-C_{14} switches from reduced to oxidized state at nearly the same speed as PEDOT in 0.1 M TBAP/CH_3CN, but takes about 3 seconds to revert back to reduced state while PEDOT takes about 10 seconds. A multiple switching study of *ca* a 250 nm thick film of PEDOT-C_{14} in 0.1 M TBAP/CH_3CN showed it to retain 40 % of its electroactivity after 1800 switches while PEDOT looses most of its electroactivity in 150 switches. In the oxidized state, PEDOT-C_{14} film was initially 60% transmissive and less than 5 % transmissive in its reduced state. After 1800 switches, the charge retention is over 50% as can be seen in Figure 3-15a and the contrast exhibited a slight drop to 55 % transmission in its oxidized form and 10 % transmission in its reduced form as can be seen from Figure 3-15b.

When the electrolyte is changed to 0.1M LiClO$_4$/CH$_3$CN PEDOT-C_8 and PEDOT-C_{14} were found to switch more rapidly. Figures 3-16a and 3-16b shows that PEDOT-C_8 reduces in less than 0.8 seconds and reoxidizes in about
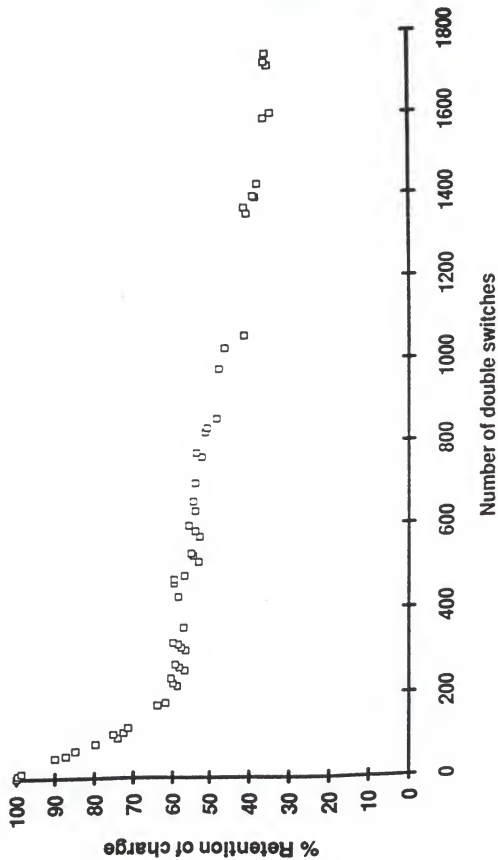
Figure 3-15a: % Retention of Charge in the long term switching studies of PEDOT-C$_{14}$ in 0.1 M TBAP/ CH$_3$CN.
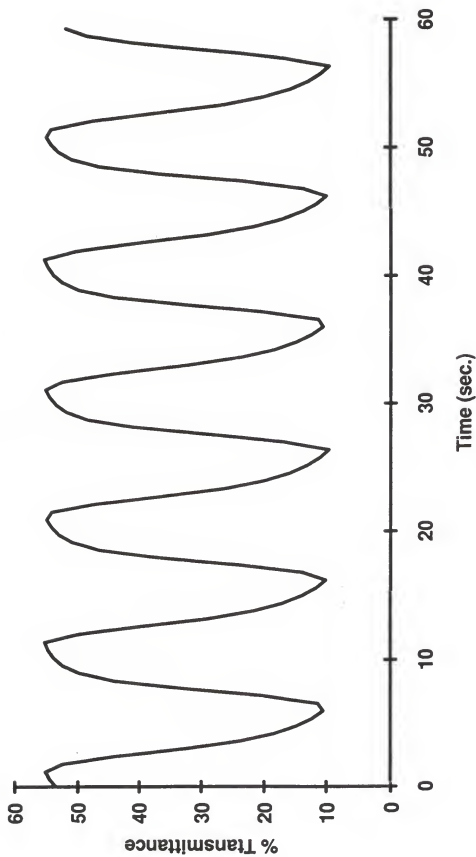
Figure 3-15b: Optical transmittance of PEDOT-C$_{14}$ in 0.1M TBAP/CH$_3$CN vs Ag/Ag$^+$. (switches 1764-1769 shown).
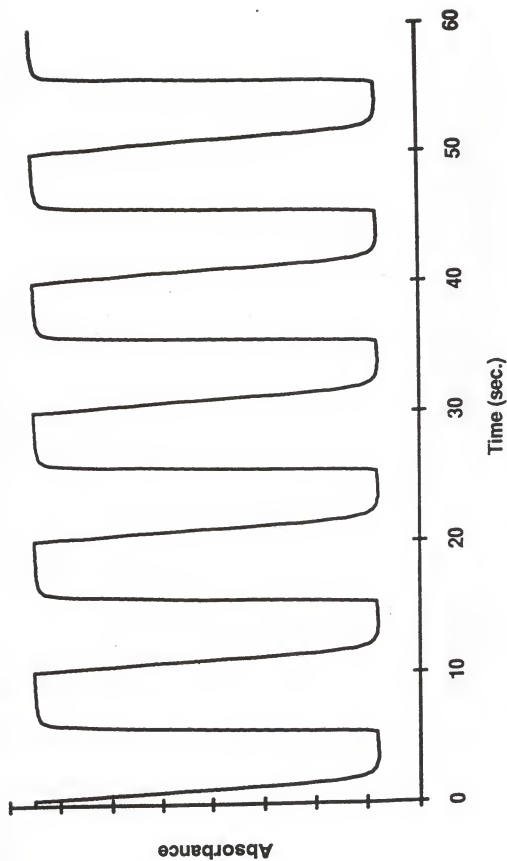
Figure 3-16a: Long term switching studies of PEDOT-C$_8$ in 0.1M LiClO$_4$/CH$_3$CN. (Switches 335-339 shown).
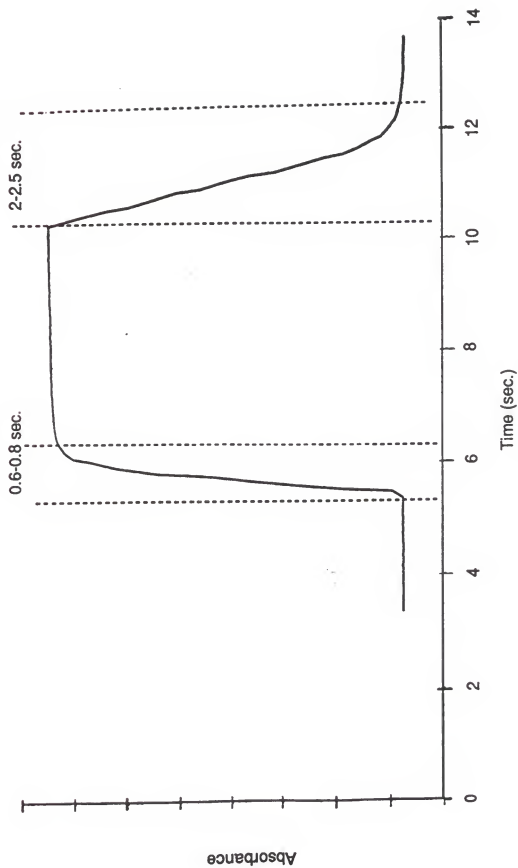
Figure 3-16b: Optical absorbance of PEDOT-C$_8$ in 0.1M LiClO$_4$/CH$_3$CN for the 335th switch

2-3 seconds. PEDOT-C_{14} shows a similar speed of switching. PEDOT also switches faster in 0.1 M $LiClO_4/CH_3CN$ as shown in Figures 3-17a and 3-17b. PEDOT-C_{14} retains more than 70 % of its electroactivity after 1100 switches in 0.1 M $LiClO_4 /CH_3CN$, while PEDOT retains less than 50 % of its electroactivity after 140 switches.

<u>3-4-2 Switching in a Completely Reversible Cell</u>

In the previous experiments, a platinum plate was used as a counter electrode and the electrochemistry occuring at this electrode was ignored. Electrochemical reactions at this junction is not known as platinum does not undergo redox chemistry under the experimental conditions used. At the redox potential of the electrochemical cell for the polymeric system, the reaction at the counter electrode can lead to formation of ions, radicals or decomposition products that can be detrimental to the life of the cell, and to the life of polymer under investigation. Hence, to have a well defined electrochemical reaction at the counter electrode, a Li electrode was chosen.[102]

The two half reactions that make up the electrochemical cell can be denoted as

$$PEDOT \rightleftharpoons PEDOT^+ + e^-$$
$$Li^+ + e^- \rightleftharpoons Li^{\circ}$$
$$PEDOT + Li^+ \rightleftharpoons PEDOT^+ + Li^{\circ}$$
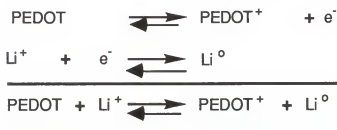
Due to the reactivity of lithium, this experiment was carried out in the dry-box under argon. It should be noted that the use of Li in commercial batteries is quite common, making these studies practically important, in addition to providing two reversible redox couples. Propylene carbonate was the solvent
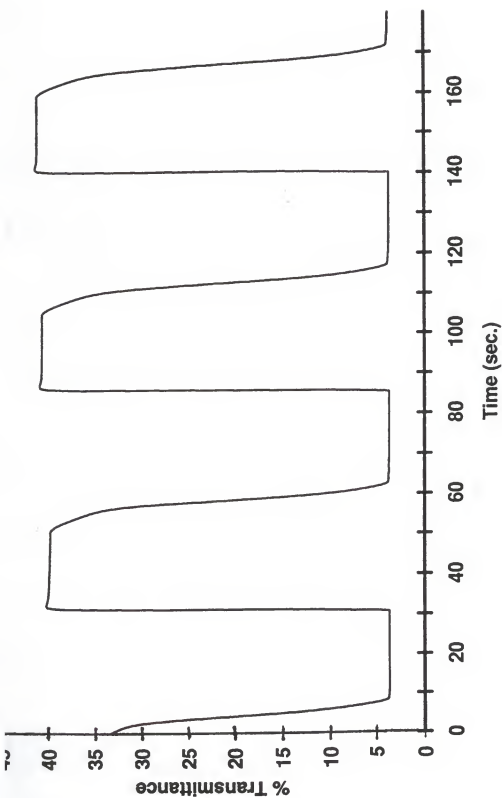
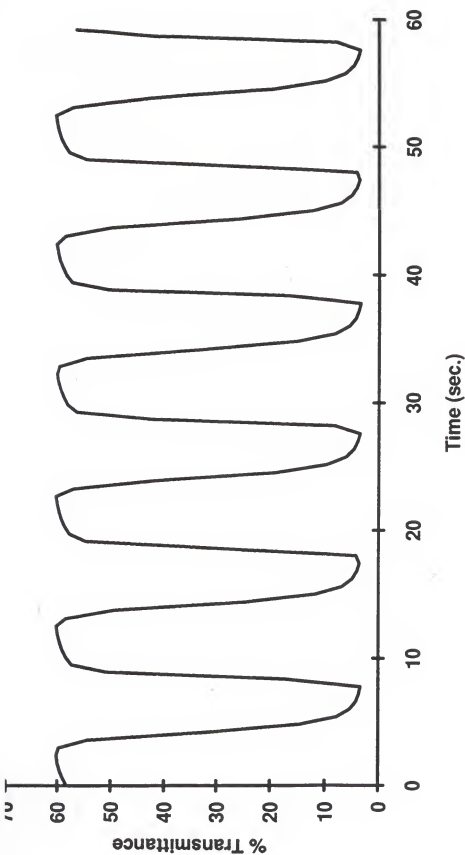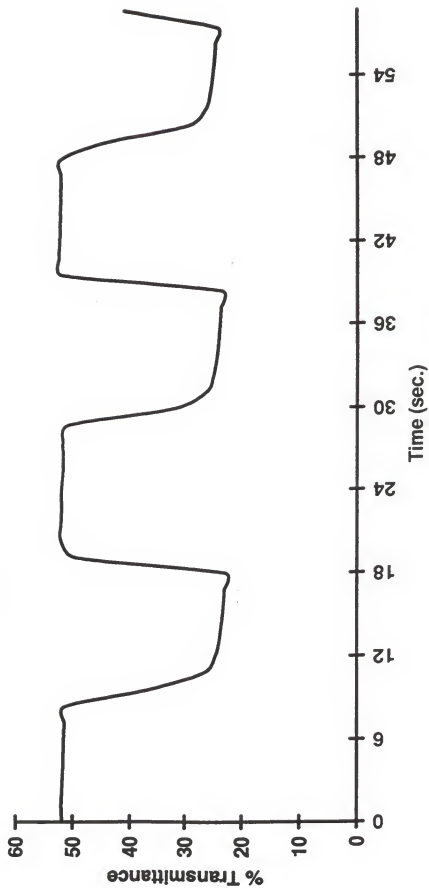Figure 3-17a: Long term switching studies of PEDOT in 0.1M LiClO₄/CH₃CN.
(Switches 18-24 shown).
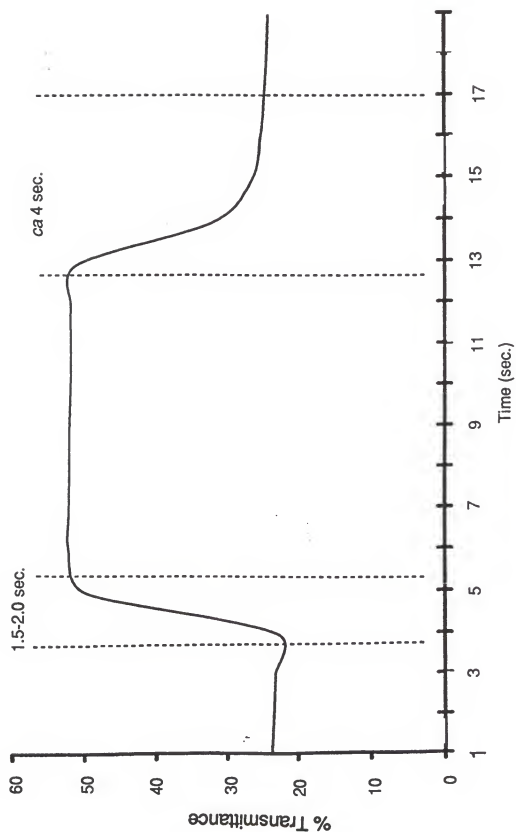
Figure 3-17b: Optical transmittance of PEDOT in 0.1M LiClO$_4$/CH$_3$CN for the 19th switch
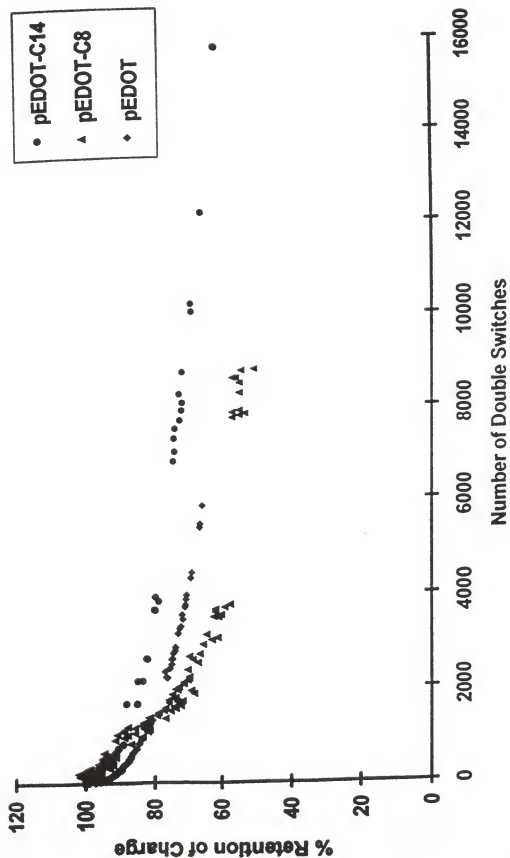
Figure 3-18: Long term switching studies of PEDOT, PEDOT-C$_8$ and PEDOT-C$_{14}$ in 0.1M LiClO$_4$/PC with Lithium as counter electrode.

used with $LiClO_4$ as the electrolyte. The polymer films were grown by passage of -150 mC through the ITO coated glass electrode outside the dry-box under argon blanket, with similar set of conditions described in the previous experiment. Ag/Ag^+ was used as a reference for PEDOT and PEDOT-C_{14}, while Ag wire was used for PEDOT-C_8.

PEDOT was switched by stepping the potential between -1.1 V to + 1.1 V with a switching interval of 10 seconds. PEDOT-C_8 and PEDOT-C_{14} were switched between -0.8 V and 0.6 V with a switching interval of 5 seconds. The change in charge was monitored as shown in Figure 3-18. Under these conditions all three polymers showed excellent retention of its electroactivity with a high degree of switchability. One switch duration in the Figure 3-18 is the 10 seconds required to switch from reduced to oxidized state and back for PEDOT-C_8 and PEDOT-C_{14} while it is 20 seconds for PEDOT for similar switch. PEDOT-C_8 was switched over 9000 times with a retention of 50 % of its electroactivity while PEDOT retained 65 % of its electroactivity with 6000 switches. PEDOT-C_{14} retained over 62 % of its electroactivity even after 16000 switches. This high retention of electroactivity even after thousands of switches forbodes potential commercial application.

3-5 An attempt to find the Molar Absorptivity of PEDOT, PEDOT-C_8 and PEDOT-C_{14} Films.

The molar absorptivities of the EDOT, EDOT-C_8 and EDOT-C_{14} monomers at the λ_{max} (600 nm) for the electronic transition were measured in $LiClO_4/CH_3CN$ electrolyte solutions and found to be 338, 420 and 343 L mol^{-1} cm^{-1} respectively. Since the polymers are insoluble, they were examined as solid films deposited on ITO glass to determine their molar absorptivities. The

polymer films were completely reduced before their absorbances were recorded.

In conjugated polymer systems, few studies have been directed towards the quantification of their UV-Vis absorption properties, since the chromophoric unit responsible for the absorption is not well defined. While this has not impeded their study, applications, such as electrochromism, could be better understood, when the amount of light absorbed can be determined. In this section, an estimation of molar absorptivity (ε) of the polymers, based on the monomer repeat , is presented as a means of comparing various polymer films.

A modified form of Beer-Lambert's law has been used to determine the molar absorptivities of the polymers.

Molar absorptivity (ε) can be denoted as

$$\varepsilon = \frac{A}{C \cdot l} \tag{1}$$

where A= absorbance, C = concentration(mole.L^{-1}) and l = pathlength of light (cm) travelling through the chromophoric media. ε has units of L.mol^{-1}.cm^{-1}. It can be seen that

$$\varepsilon = \frac{A}{\frac{M}{V} \cdot l} = \frac{A \cdot V}{M \cdot l} \tag{2}$$

where M = moles of chromophore and V = volume. Since in these studies, polymer films are being used, as opposed to a solution, the volume and moles of the repeat unit in the film can be applied and determined using equations 3 & 4.

$$V = a \cdot t \tag{3}$$

Here, a is the area of the polymer which interacts with light, and t is the thickness of the polymer film.

$$M = \frac{m_s}{m_w} \tag{4}$$

m_s = mass of the sample, m_w = molecular weight of the repeat unit.

Substituting V and M into equation (2) gives

$$\varepsilon = \frac{A \cdot (a \cdot t) \cdot m_w}{m_s \cdot l} \qquad (5)$$

All of the variables in equation (5) are experimentally measurable allowing a value of ε to be determined. The amount of polymer interacting with the light is a function of film thickness and mass. It can be seen that, volume and mass can be represented in terms of density, (d).

$$d = \frac{m_s}{a \cdot t} \qquad (6)$$

Thus equation (5) simplifies to (7)

$$\varepsilon = \frac{A \cdot m_w}{d \cdot l} \qquad (7)$$

Since all of the chromophoric units are in the polymer film, the thickness (t) of the film can be considered as the pathlength of light interacting (l). Simplifying, equation (5) becomes to equation (8).

$$\varepsilon = \frac{A \cdot a \cdot m_w}{m_s} \qquad (8)$$

After determination of polymer density (d), or the specific area (a) interacting with the light, the only experimental values to be measured are absorbance (A), mass (m_s) and thickness (t) of the polymer films. Density of the films were determined by flotation as described in section 3-6-2. The area of the projected light was measured directly and a profilometer used to find the thickness of the films. The thicknesses of the films ranged from 200 to 300 nm

(+/- 50nm) and significant errors were incurred using this method due to the non-uniformity of the film. Film masses were on the order of 50 to 75 μg and could be weighed accurately to +/- 10 μg. From flotation, densities of 1.72, 1.27, and 1.05 g/ml for PEDOT, PEDOT-C_8 and PEDOT-C_{14} respectively were determined. These densities confirm the fact that films of PEDOT-C_{14} have a more porous morphology than PEDOT-C_8 and PEDOT films is most well-packed among these three polymers. These led to molar absorptivities for the PEDOT, PEDOT-C_8 and PEDOT-C_{14} polymers, at λ_{max} of 1.5×10^3, 3.1×10^4, and 5×10^4 respectively when equation (8) is used. A sample calculation is illustrated in Figure 3-19. The ε values determined by both the methods are reasonably similar as reviewed in Table-3.

While this method is approximate, it still provides an insight into the relative molar absorptivity of the polymers studied. Molar absorptivities of these EDOT polymers are approximately an order of magnitude higher than their respective monomers. The values of ε obtained for this polymer series is as expected for a π to π^* electronic transition. Application of this technique in the future to other electrochromic polymers should provide reasonable comparisons of the properties of various materials.

3-6 Experimental

3-6-1 Electrochemistry

Cyclic voltammetry was conducted utilizing platinum button working, platinum plate counter and Ag/Ag$^+$ reference electrodes. Potentials were controlled using a PAR EG&G model 273 potentiostat/galvanostat. Polymer films for optoelectrochemical measurements were prepared on ITO coated glass slides (Delta Technologies) as the working electrode.

Sample calculation of E for **PEDOT** for:
A = 0.6,
Area of slit = 0.28 cm^2,
Molecular weight of the repeat unit = 140.03
thickness of film = 200 nm,
density = 1.73 gm/cc,
$m_s = 1.6 \cdot 10^{-5}$ gm

By using Eqn. 4

$$E = \frac{A \cdot a \cdot mw}{m_s}$$

since $V = a \cdot t \ cm^3 = \frac{a \cdot t}{1000}$ litres

$$E = \frac{0.6 \cdot 140.03 \cdot 0.28}{(1.6 \cdot 10^{-5}) \cdot 1000}$$

$$E = 1.48 \times 10^3 \ L \ mol^{-1} \ cm^{-1}$$

By using Eqn. 3

$$E = \frac{A \cdot mw}{d \cdot l}$$

$$= \frac{0.6 \cdot 140.03}{200 \cdot 10^{-7} \cdot 1000 \cdot 1.73}$$

$$E = 2.43 \times 10^3 \ L \ mol^{-1} \ cm^{-1}$$

Figure 3-19: Sample calculations for molar absorptivity of PEDOT.

Table 3. Molar aborptivity of the polymers in 0.1 M LiClO$_4$/ CH$_3$CN vs 0.01 M Ag / Ag$^+$

Polymer films	Abs.[a]	Density gm/cc	Molar Absorptivity (ϵ) by using Equation (7) L.mol^{-1}cm^{-1}	Molar Absorptivity (ϵ) by using Equation (8) L.mol^{-1}cm^{-1}
PEDOT	0.6	1.73	$2.4 * 10^3$	$1.5 * 10^3$
PEDOT-C$_8$	1.4	1.27	$1.1 * 10^4$	$3.1 * 10^4$
PEDOT-C$_{14}$	2.5	1.05	$2.7 * 10^4$	$5.0 * 10^4$

[a] Absorbance in their totally reduced state.

Tetrabutylammonium perchlorate (TBAP) and lithium perchlorate (LiClO$_4$) were used as electrolytes in electochemical studies. Optoelectronic spectra were obtained using a Varian Cary 5E UV-Vis-NIR spectrophotometer.

3-6-2 Determination of Density of PEDOT and its Alkyl derivatized polymers

Flotation method was employed to determine the density of these polymers.[103] The polymers were grown on an ITO coated glass electrode and reduced to its neutral form. Small pieces of the film was scraped off from the ITO plate were used to get a reasonably accurate density of the polymers. For PEDOT, CHCl$_3$ and 1,2-dibromoethane was used to determine the density and it was found to be 1.73 gm/cc. For PEDOT-C$_8$, toluene with a density of 0.867 and 1,2-dibromoethane were used to obtain the required equilibrium volume of the solvent mixture and the calculated density was 1.27 gm / cc. For PEDOT-C$_{14}$, hexane with a density of 0.660 and 1,2-dibromoethane were used as the solvent mixture and the calculated density was 1.05 gm / cc.

3-6-3 Long Term Switching Studies

CH$_3$CN was freshly distilled over CaH$_2$. TBAP was recrystallized from ethylacetate. LiClO$_4$ was recrystallized from CH$_3$CN and the dried salt was melted at 110 °C under vacuum, held for 24 hrs and subsequently slowly cooled to under vacuum. Propylene carbonate was stored over 4 A° molecular sieves for 2 days, before distilling it with fresh sieves under vacuum. This distilled solvent was kept over molecular sieves in argon at all times.

In the electrochemical cell used, ITO coated glass electrode was used as working electrode, platinum plate and 0.01 M Ag/Ag$^+$ as the counter and

reference electrode respectively. The solvents were purged with argon before use and a blanket of argon was maintained on the electrochemical cell at all times during the growth of the polymer. The polymer was grown on the ITO coated glass electrode at constant potential to approximately -150 mC for all three of the polymers. PEDOT was grown at 1.2 V whereas PEDOT-C_8 and PEDOT-C_{14} were grown at 1.0 V. The polymers were washed with monomer free electrolyte solution before carrying the long term switching studies.

3-6-4 Preparation of Reversible cell for Long Term Switching.

Figure 3-20 illustrates the reversible cell used for long term switching studies. The counter electrode in this cell was Li instead of the normal platinum. Lithium elecrodes were prepared in the dry-box. Lithium metal was flattened into a thin sheet and wrapped around a platinum wire, covering approximately the lower half of the wire. This was enclosed in a glass jacket with a opening on both the ends, the lower end with a smaller circumference. The lower end was dipped into the electrolyte solution of the electrochemical cell, while the other end with the platinum was used as the contact for the cell. The lithium part was completely immersed into the electrolyte solution. The working electrode was ITO coated glass electrode with polymer deposited on it and the reference electrodes were Ag wire or Ag/Ag+.

3-6-5 Materials and Methods for Synthesis

Thiodiglycollic acid, diethyl oxalate, DMF (anhydrous), bromine, dodecene, hexadecene, KOH, copper chromite were used as purchased from Aldrich without any further purification. Absolute ethanol was bought from Aaper Alcohol and Chemical Co. K_2CO_3 was dried under vacuum overnight at
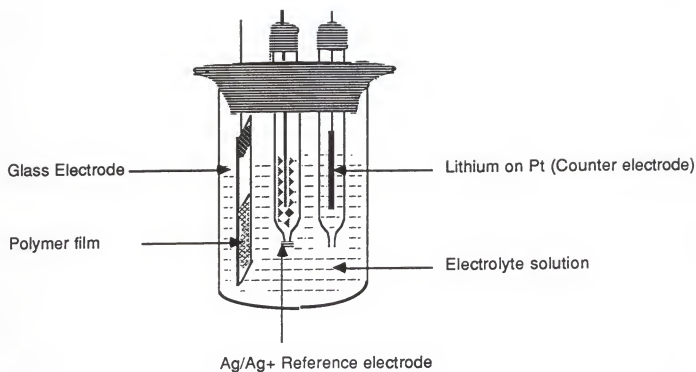
Figure 3-20: Electrochemical cell for long term switching studies of
PEDOT series with lithium as the counter electrode.

110 °C. Quinoline was dried in Na_2SO_4 and vacuum distilled over zinc dust. Absolute ethanol was used without any purification. Characterization was done by using ^1H and ^{13}C NMR spectroscopy from Varian Gemini-300, Varian XL-300 FTNMR, FTIR and Mass Spectrometer. Elemental analysis was done at Atlantic Microlab Inc and Robertson Microlit Laboratories, Inc.

3-6-6 Synthesis of EDOT and EDOT-C$_8$ and EDOT-C$_{14}$, monomers

3-6-6-1 Synthesis of diethylthioglycollate (1)[100]

300 gms of thiodiglycollic acid was esterified with the help of 2 ml of H_2SO_4 as a catalyst in presence of 1000 ml of absolute ethanol in 2 liter, one necked round bottomed flask fitted with a condenser and drying tube. After refluxing the reaction mixture for 12 hrs nearly 700 ml. of ethanol and water was azeotropically distilled. 500 ml of fresh, absolute ethanol was added and refluxed for 20 more hours. The mixture was washed with water to remove ethanol and acid, extracted the aqueous with ether, combined and dried the organic layer and concentrated to get nearly quantitative yield. This was vacuum distilled to yield colorless liquid with a strong sulfurous odor. Yield 637 g, 91%.

3-6-6-2 Disodium salt of 2,5-dicarboethoxy-thiophene-3,4-dioxide (2)[100]

Sodium ethoxide was freshly prepared by dissolving, in portions 32.7 gms of Na in 1500 ml of absolute ethanol in a 3 liter flask fitted with a mechanical stirrer and a 250 ml dropping funnel under a blanket of argon. Slowly a mixture of 115 gms (0.558 mol) of **1** and 83.5 gms (0.571 mol) in 50 ml of absolute ethanol was added into the reaction vessel dropwise, with the help of dropping funnel, overnight with constant stirring. Thick curdy yellow precipitate of the disodium salt was formed immediately. The mixture was warmed for 2 hrs to 50 °C to complete the reaction. The solution was vacuum

filtered in a buchner funnel, washed with ethanol and air dried to yield finely powdered bright yellow precipitate quantitatively.

3-6-6-3 2,5-Dicarboethoxy-3,4-dihydroxythiophene (3)[100]

The disodium salt **2** (100 g, 0.357 mol) was dissolved in 1500 ml of distilled water and 300 ml of 1 M HCl was added slowly dropwise with constant stirring till the solution became acidic. Immediately thick white curd precipitated fell out. The product was filtered and washed with water and air dried. Recrystallization from ethylacetate yielded a white shiny solid at 86% yield (72.5 g). M. P. 130-132°C. ^{1}H NMR (δ, ppm, TMS reference); 1.35 (t), 4.35 (q), 9.36 (s). ^{13}C NMR; 14, 62.0, 107, 152, 166.

3-6-6-4 2,5-Dicarboethoxy-3,4-ethylenedioxythiophene (4a)[100]

3 (3.8 mmol) was refluxed at 90 °C with 1, 2-dibromoethane (3.8 mmol) and anhydrous K_2CO_3 (9.6 mmol) in anhydrous DMF for 24 hrs. This yielded a burgundy viscous liquid with some yellow solids at the bottom of the flask. The reaction mixture was cooled and poured into 50 ml of hot acetone, stirred for 10 minutes and filtered. The filtrate was added into 50 ml of pentane, washed repeatedly with dilute HCl and water to remove DMF, dried and concentrated. Recrystallization from ethylacetate yielded a white solid. Yield 70 %.(0.76 g) ^{1}H NMR (δ, ppm, TMS reference); 1.35 (t, $J = 7$ hz), 4.35 (q, $J = 8$ hz), 4.4 (s). ^{13}C NMR; 16, 61.0, 62.5, 112, 145, 161. Mass Spectrometer: molecular ion peak, 287 amu.

3-6-6-6 2,5-Dicarboxy-3,4-ethylenedioxythiophene (5a)[100]

4a (0.5 g, 1.7 mmol) was added to an excess amount of aqueous solution of 5% NaOH and refluxed. The solid slowly dissolved after refluxing for 6 hour. The solution was cooled and acidified with conc. H_2SO_4 till the solution became very acidic. The product precipitates at a low pH. The solution was cooled in the freezer to complete precipitation, filtered, washed with water and

oven dried to yield 0.29 g of white solid. Yield 74 %. ^{1}H NMR (δ, ppm, TMS reference); 4.3 (s), 13.2 (b). ^{13}C NMR; 62.5, 112.0, 143.5, 162.0. Mass Spectrometer: molecular ion peak, 231 amu.

3-6-6-7 3,4-Ethylenedioxythiophene (6a)[100]

1 g (4.3 mmol) of **4a** was refluxed in quinoline with 4 % copper chromite as a catalyst at 160 °C for 6 hrs under an argon atmosphere. The reaction mixture was cooled, added into 25 ml of pentane, stirred and filtered through celite. The filtrate was washed repeatedly with water and 1M HCl. After air drying, flash chromatography, the filtrate yielded a colorless liquid. (Yield 0.63 g, 48%). ^{1}H NMR (δ, ppm, TMS reference); 4.2 (s), 6.32 (s). ^{13}C NMR; 65, 110, 142.

3-6-6-8 2,5-Dicarboethoxy-5-octyldioxeno[2,3-c]thiophene (4b)

10 g (0.038 mol) of the dihydroxy compound **3** was dissolved in 80 ml of anhydrous DMF in a 250 ml 3NRBF under argon. 12 g (0.087 mol) of K_2CO_3 and 13 g (0.044 mol) of 1,2-dibromodecane (prepared from 1-decene and bromine) was introduced and the mixture was heated to 110 °C for 48 hrs. The reaction mixture was cooled, stirred with 100 ml of diethyl ether and the dark brown liquid filtered. The filtrate was washed with de-ionized water, and the aqueous portion was extracted with ether. The organic solutions were combined, dried and concentrated to yield whitish brown solid. Recrystallization from ether yielded a white, powdery solid. Yield 15.1 g, 52.2 %. M. P. 92 - 94 °C. Anal. Calcd: C, 60.32; H, 7.53; S, 8.03; O, 28.04. Found: C, 60.25; H, 7.46; S, 8.02; O, 27.67. ^{1}H NMR (δ, ppm, TMS reference); 0.71 - 0.99 (t), 1.09 - 1.92 (m), 3.92 - 4.13 (dd, J = 10, 11 hz), 4.17 - 4.55(m). ^{13}C NMR; 14.0, 14.04, 22.65, 24.99, 29.21, 29.40, 29.46, 30.66, 31.83, 61.5, 68.47, 112, 112.5, 141.72, 142.21, 161. Mass Spectrometer: molecular ion, 398.19 amu; base peak , 213.99 amu.

3-6-6-9 5-Octyldioxeno[2.3-c]thiophene-2.5-dicarboxylicacid **(5b)**

The diester **4**, 0.7 g (1.8 mmol) was hydrolyzed by refluxing in 30 ml of 10 % KOH for 8 hrs, when all of **4** dissolved. The reaction mixture was cooled and added drop-wise into 100 ml of 0.1 M HCl. The milky white precipitate was collected by vacuum filtration, washed with copious amount of water and dried. Yield 74 % (0.62 g) M.P. 216 - 220 °C. Anal Calcd: C, 56.13; H, 6.5; S, 9.36. Found: C, 55.92; H, 6.43; S, 9.66. ^{1}H NMR (δ, ppm, TMS reference); 0.75 - 0.96 (t), 1.11 - 1.75 (m), 4.04 (dd, J = 12, 7.5 hz), 4.29 (d, J = 7.5hz), 4.41(d, J = 9 hz), 13.1(b). ^{13}C NMR; 13.97, 22.13, 24.29, 28.65, 28.81, 28.89, 29.65, 31.31, 67.46, 73.70, 111.42, 111.53, 144.61, 144.87, 161.79. Mass spectrometer : molecular ion peak, 342.11 amu, base peak, 55.07 amu.

3-6-6-10 2.5-Dicarboethoxy-5-tetradecyldioxeno[2.3-c]thiophene **(4c)**

8.3 g (0.039 mol) of the dihydroxy compound **3** was dissolved in 80 ml of anhydrous DMF in a 250 ml 3NRBF under argon. 11 g (0.080 mol) of K_2CO_3 and 13.5 g (0.035 mol) of 1,2-dibromohexadecane (prepared from 1-hexadecene and bromine) was introduced and the mixture was heated to 90 °C for 48 hrs. The reaction mixture was cooled to room temperature, stirred with 100 ml of boilingt diethyl ether, and the dark brown liquid filtered. The filtrate was washed with de-ionized water; the aqueous layer was extracted with ether. The organic solutions were combined, dried and concentrated yielded a whitish brown solid. Recrystallization from a 4:1ether and methanol mixture to yield whitish particulate solid. Yield 4.5 g, 24 %. M. P. 70-74 °C. Anal Calcd: C, 64.77; H, 8.77; S, 6.63. Found: C, 65.27; H, 9.06; S, 6.53. ^{1}H NMR (δ, ppm, TMS reference);0.9 (t), 1.2 - 1.85 (m), 3.9 - 4.8 (m). ^{13}C NMR; 14.08, 14.26, 22.69, 24.92, 29.35, 29.41, 29.53, 29.65, 30.41, 31.93, 61.14, 61.22, 68.40, 74.25, 128.51, 145.02, 160.90. Mass Spectrometer: molecular ion peak, 482 amu; base peak, 55 amu.

3-6-6-11 5-Tetradecyldioxeno[2.3-c]thiophene-2.5-dicarboxylic-acid (5c)

21 g (0.044 mole) of the diester **4c**, was hydrolyzed by refluxing in 150 ml of 10 % KOH for 12 hrs. The reaction mixture was cooled; and the solid that was formed in the reaction filtered off. The filtrate was added drop-wise into 500 ml of 0.1 M HCl. The milky white precipitate was collected by vacuum filtration, washed with copious amount of water and oven dried. Yield 7.2 g, 39 %. Anal Calcd: C, 61.95; H, 8.03; S, 7.50. Found: C, 59.04; H, 7.61; S, 7.87. ^{1}H NMR (δ, ppm, TMS reference); 0.9 (t), 1.18 - 1.6 (m), 3.95 - 4.45(m), 13.1(b). ^{13}C NMR; 14.84, 23, 25.19, 29.51, 29.63, 29.69, 29.80, 29.87, 29.96, 30.59, 32.22, 68.42, 74.65, 112.37, 112.5, 145.51, 145.76, 162.64. Mass spectrometer: molecular ion peak, 426 amu; base peak, 55 amu.

3-6-6-12 5-Octyldioxeno[2.3-c]thiophene (6b)

A mixture of **5b** (1 g, 0.003 mol) and 15% by mole of copper chromite, as a catalyst, were taken in a 500 ml 1NRBF with 100 ml of freshly distilled quinoline and heated to 150 °C for 24 hrs. After cooling to room temperature, 100 ml of pentane was added, stirred and the solid catalyst filtered off through celite. The quinoline was washed from the organic filtrate by repeated washing with 1M HCl till the pH of the aqueous layers was acidic. The organic layer was washed with 1M NaHCO$_3$ and water till neutral. After air drying, the organic layer was concentrated and flash chromatography yielded a pale yellow liquid. Yield 0.56 g, 87 %. Anal Calcd. C, 66.01; H, 8.70; S, 12.57. Found. C, 66.10; H, 8.56; S, 12.11. ^{1}H NMR (δ, ppm, TMS reference); 0.883 (t), 1.2 -1.8 (m), 3.8 - 4.2(m), 6.3(s). ^{13}C NMR; 14.1, 22.65, 24.98, 29.21, 29.20, 29.40, 29.46, 30.66, 31.83, 68.47, 73.79, 99.20, 99.24, 141.72, 142.21. Mass spectrometer: molecular ion and base peak at 255.

3-6-6-13 5-Tetradecyldioxeno[2,3-c]thiophene **(6c)**

A mixture of **5c** (1 g, 2,3 mmol) and 15% by mole of copper chromite, as a catalyst, were taken in a 500 ml 1NRBF with 100 ml of freshly distilled quinoline and heated to 150 °C for 24 hrs. The reaction mixture was cooled, added to 100 ml of pentane, stirred and the solid catalyst filtered off through celite. The quinoline was removed from the organic filtrate by repeated washing with 1M HCl till the pH of the aqueous layers was acidic. The organic layer was washed with 1M $NaHCO_3$ and water till neutral. After drying the organic layer was concentrated and flash chromatography yielded a whitish gray solid. Yield 0.3 g, 38 %. Anal Calcd. C, 70.97; H, 10.12; S, 9.4. Found. C, 71.08; H, 10.31; S, 7.87. ^{1}H NMR (δ, ppm, TMS reference); 0.88 (t), 1.2 - 1.7 (m), 3.7 - 4.2 (m), 6.29. ^{13}C NMR; 15.2, 22.6, 22.7, 25.0, 29.2, 29.3, 29.4, 29.42, 29.44, 29.5, 29.7, 30.65, 31.8, 31.9, 68.2, 74.0, 99.8, 99.9, 142.0, 142.5. Mass spectrometer: molecular ion peak, 338 amu; base peak, 55 amu.

CHAPTER 4
CONCLUSIONS

Heteroaromatic polymers like polythiophene, polypyrrole, polyfuran, polyaniline, and polycarbazole are electroactive materials. These polymers are continuosly being derivatized to obtain materials with better properties. One of the goals in synthesizing new molecules with good π overlap is to obtain monomers and polymers with lower oxidation potentials and band gaps. Polythiophene, which has an adequate stability in both its oxidized and reduced states, compared to other known electroactive polymers under ambient conditions, is the material of choice to study its changes in properties through derivatization, which would lead to better material. Synthesis of new derivatized thiophene polymers are described in this dissertation. Two different approaches have been applied to make materials having better electroactive properties. The first approach was to synthesize a symmetrically derivatized thiophene monomer, 1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene, which would lead to regio-regular polymers. The second approach was to attach a cyclic electron donating group at the 3 and 4 positions of thiophene to produce 3,4-ethylenedioxythiophene and its alkyl derivatives, to obtain lower oxidation potential monomers and polymers and materials with lower band gaps.

4-1 Poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylenes]

1,4-Bis(2-thienyl)-2,5-dicyclohexylmethyloxybenzene has been synthesized and polymerized chemically and electrochemically. $FeCl_3$ induced oxidative polymerization in chlorinated solvents, followed by NH_4OH compensation, yields a totally insoluble brick-red polymer. Thermogravimetric analysis of poly[1,4-bis(2-thienyl)-2,5-dicyclohexylmethyloxyphenylene] shows no weight loss up to 400°C. Electropolymerization in CH_3CN with tetrabutylammonium perchlorate yields electroactive and conducting films. Cyclic voltammetry of the monomer showed two redox processes during the polymerization. The first redox process has an onset at 0.8 V (peak = 0.9 V), while the second has an onset at 1.0 V (peak = 1.1 V) versus Ag/Ag^+. When the potential is scanned to 0.9 V, very slow film formation is observed by cyclic voltammetry. Increasing the switching potential of the scan up to 1.1 V leads to an increase in the rate of film formation by nearly 25 times. This polymer is stable to electrochemical switching up to 1.1 V and becomes electrochemically inactive above that potential. Optoelectrochemical studies showed that the highly oxidized polymer has only one absorbance in the NIR suggesting a metallic-like character.

4-2 Poly(3,4-ethylenedioxythiophene) and its octyl and tetradecyl derivatives

It is known that attaching electron donating groups to conjugated systems lowers oxidation potentials and band gaps. Thiophene has an oxidation potential around 2 Volts vs Ag/Ag^+. Cyclic voltammetric electropolymerization of EDOT, EDOT-C_8 and EDOT-C_{14} in 0.1M TBAP/CH_3CN show monomer oxidation peaks ($E_{a,p}$) of 1.0 V, 0.89 V and 0.93 V respectively, yielding

electroactive and conducting polymer films. PEDOT synthesized chemically or electrochemically yielded blue-black insoluble powder. Octyl and tetradecyl substituents were attached to improve the polymer solubility. The oligomers of PEDOT-C_8 and PEDOT-C_{14} are soluble, but the polymers are only partially soluble in common organic solvents.

The attachment of the alkyl chain, in the PEDOT-C_8 and PEDOT-C_{14} derivatives leads to the formation of electroactive polymer films with a loose morphology. This makes it easier for the movement of ions into and out of the polymer films during redox cycling. Density measurements revealed that the films of PEDOT are the most dense, presumably due to more interchain interactions and better packing without the long alkyl chains, while PEDOT-C_{14} is the least dense, due to the long alkyl chain, resulting in fewer interchain interactions among the three polymers. This correlates well with the switching speed and stability of the polymer films. When the polymer films are redox switched, the polymer chain has to distort to accomodate the counter ions that move in and out of the polymer films. Since PEDOT is the most dense, it requires more time to reach equilibrium when redox switched, and more distortion from its original structure must occur relative to PEDOT-C_8 and PEDOT-C_{14}. This larger distortion of the polymer chains in PEDOT leads to the loss of its electroactivity faster than PEDOT-C_8 and PEDOT-C_{14} in all the electrolyte/solvent systems used to study in this dissertation. These films are opaque, dark blue when they are reduced and transparent light blue when oxidized. The easier movement of the counter ions in PEDOT-C_8 and PEDOT-C_{14} helps in complete oxidation and reduction of these films. Hence PEDOT-C_8 and PEDOT-C_{14} show high optical contrast between their two states, as shown in Figure 4-1. This contrast can be exploited in making electrochromic devices. The electrochemical cell can be improved by replacing the platinum

Oxidized transparent   Reduced opaque
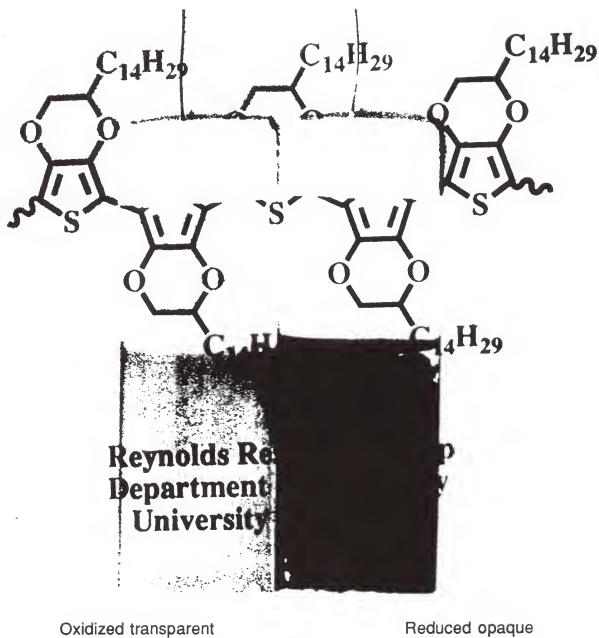
Figure 4-1. Oxidized and reduced states of PEDOT-C_{14} films grown to similar charge densities.

counter electrode with a lithium electrode, resulting in increased stability of these electroactive films, which were able to be switched thousands of times.

Molar absorptivity studies of PEDOT, PEDOT-C$_8$ and PEDOT-C$_{14}$ showed the substituted derivatives to have higher ε values compared to the unsubstituted polymer. The ε values for these polymers are over an order of magnitude higher compared to their monomers.

All of the thiophene derivatized polymers studied in this dissertation display only one absorption at higher oxidation potentials in the optoelectrochemical experiments. This suggests that all of them have a metallic-like character at higher oxidation potentials.

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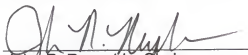
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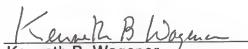
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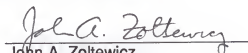John R. Reynolds, Chair
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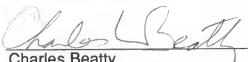
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May, 1996

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